A multiscale link between atomistic and continuum hydrodynamics via adaptive coarse-graining.

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Coworkers

- *MD-DPD-continuum*.
  - **Kurt Kremer**, Max-Plank Institute for Polymer Research (Mainz, Germany).
  - **Matej Praprotnik**, Max-Plank Institute for Polymer Research.

- *MD-continuum hydrodynamics*
  - **Gianni De Fabritiis**, U. Pompeu Fabra (Barcelona)
  - **Peter Coveney**, UCL (London)

- *Open boundaries for Fluctuating hydrodynamics*
  - **Anne Dejoan**, CIEMAT (Madrid)

- *Coarse-graining with proper dynamics*.
  - **Pep Español**, UNED (Madrid).

The general purpose

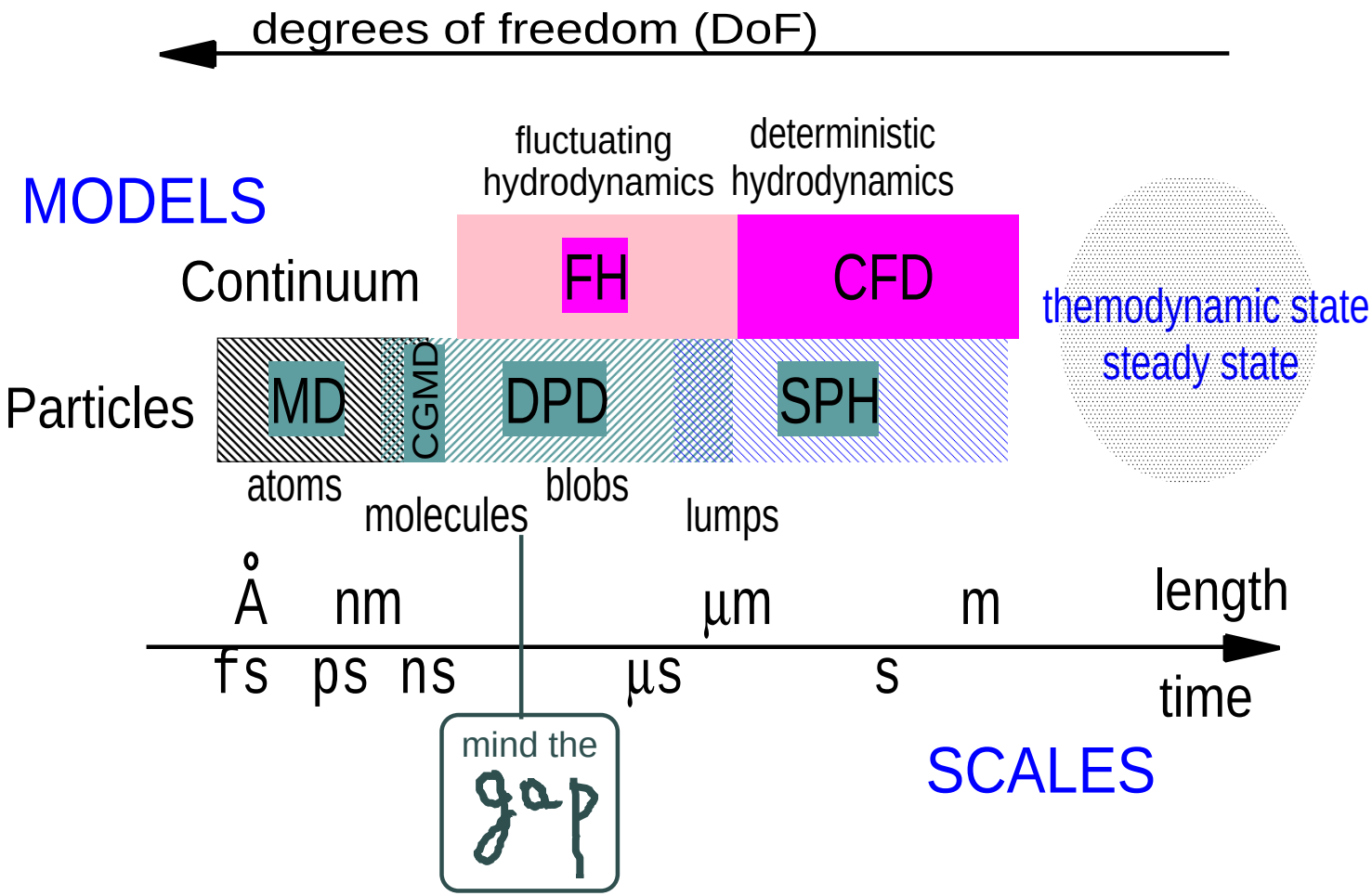
Can a better link between atomistic modeling and continuum modeling be made via DPD, thus creating a multiscale modeling protocol?

The general frame

- Dissipative: random forces and friction replaced the integrated effect of removed degrees of freedom (entropy)
- Particle: conservative forces, fluid structure (enthalpy)
- Dynamics:
  - A formulation for proper particle diffusion?.
  - Local momentum conservation upon binary collisions: Hydrodynamics.

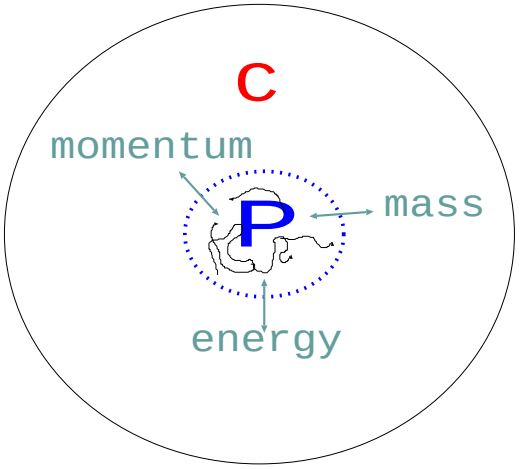
Scales and models

with hydrodynamics



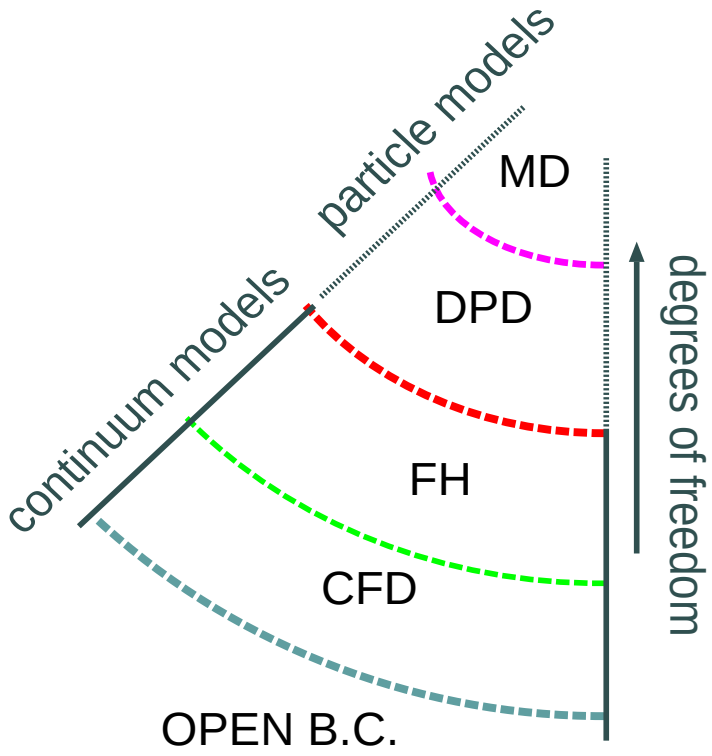
Multiscale modelling: Motivation. Applications.

- Multiscale models: predicted as a scientific milestone in near future by the 2020 Science Group. [$Nature$ **440** (7083): 383 (2006)]
- Complex fluids near interfaces: microfluidics, slip of liquid flow past surfaces.
- Fluid-fluid or soft interfaces (e.g., Rayleigh-Taylor instability, membrane's dynamics)
- Macromolecules-sound interaction (proteins) [*Science*, 309:1096, 2005.]
- Crystal growth from liquid phase.
- Wetting phenomena: microscopic treatment of the wetting front. Lubrication
- Confined systems: driven to chemical equilibrium, osmosis driven flows through membranes, thin films, water between membranes, clays,
- etc...



Domain decomposition

Interfacing models with different degrees of freedom



Open boundary conditions:
OUTSIDE WORLD
steady state,
thermodynamic reservoir

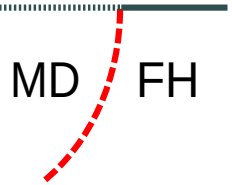
Domain decomposition

some recent works

particle - open BC

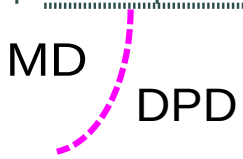
E. Flekkoy, RDB, P. Coveney, PRE (2005)

particle - continuum



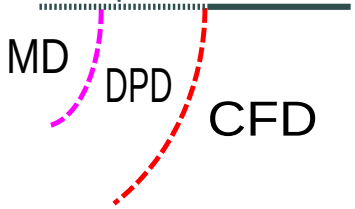
G. De Fabritiis, RDB, P. Coveney, PRL (2006)
RDB, G. De Fabritiis, PRE (2007)

particle - particle



M. Praprotnik, L. Delle Site, K. Kremer, JCP (2005)

particle - particle-continuum

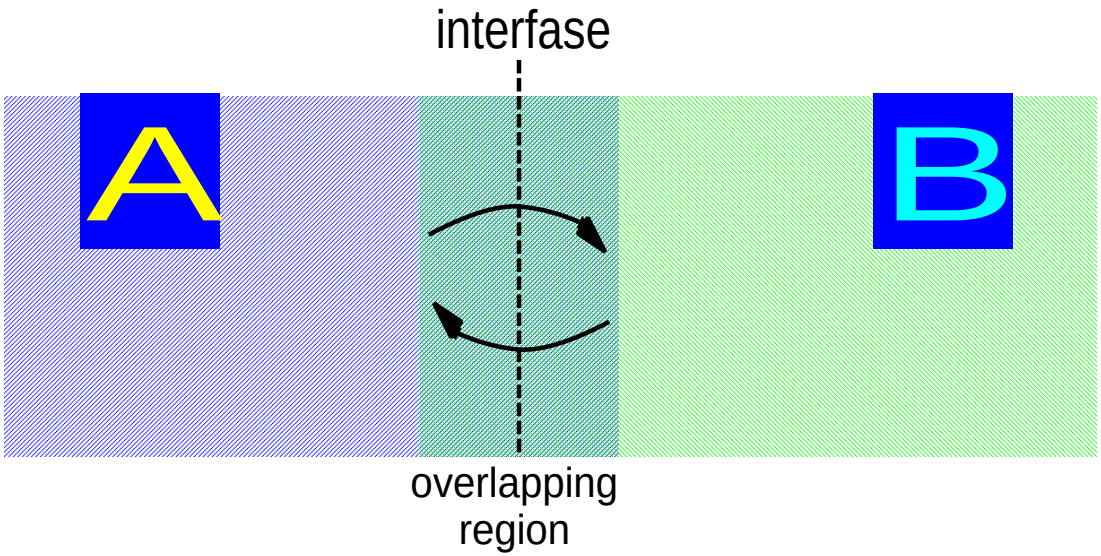


RDB, M. Praprotnik, K. Kremer JCP (2008)

open fluctuating hydrodynamics

RDB, Anne Dejoan, PRE (to appear, 2008)

Coupling two fluid models



exchanged
conserved quantities

hydrodynamic modes

momentum — transversal momentum → shear

momentum — longitudinal momentum → sound

mass → sound

energy → heat

Matching conditions

Particle-Particle coupling

- Fluid structure: radial distribution function (RDF), angular distribution functions...

- Thermodynamics

  - Equation of state (pressure-density relation).
  - Fluctuations (mass $\Longrightarrow$ grand canonical ensemble)

- Dynamics

  - Self diffusion coeffcient
  - Viscosity, etc...

Matching conditions

Particle-Continuum coupling

- Fluid structure (near the interface region)

- Thermodynamics
  - Equation of state: pressure-density relation $\Longrightarrow$ sound.
  - Fluctuations (**MD-FH**)
    - Momentum $\Longrightarrow$ Temperature
    - Stress tensor $\Longrightarrow$ Consistency in Green Kubo relations
    - Mass $\Longrightarrow$ Grand canonical

- Dynamics
  - Viscosity, thermal diffusivity.

Matching conditions

Open Boundaries

Objetive: Couple a finite, non-periodic simulation box to the thermodyamic and mechanical state at the outer world (*reservoir*).

- Avoid finite size effects present in periodic boundary conditions (e.g. sound loops)

- Evacuate waves out of the sytem (sound, heat, vortex).

- Introduce the desired amount of heat and/or work into the system $\Longrightarrow$ **generalized thermodynamic ensembles**, including thermal and velocity gradients, Joule -Thompson expansion, etc...

References:

- Particle model: Flux boundary conditions for particle simulations, E. Flekkoy, RDB, P. Coveney, *Phys. Rev. E*

- Fluctuating hydrodynamics: Open boundaries for fluctuating hydrodynamics, RDB, A. Dejoan, *Phys. Rev. E* (accepted)

Particle models

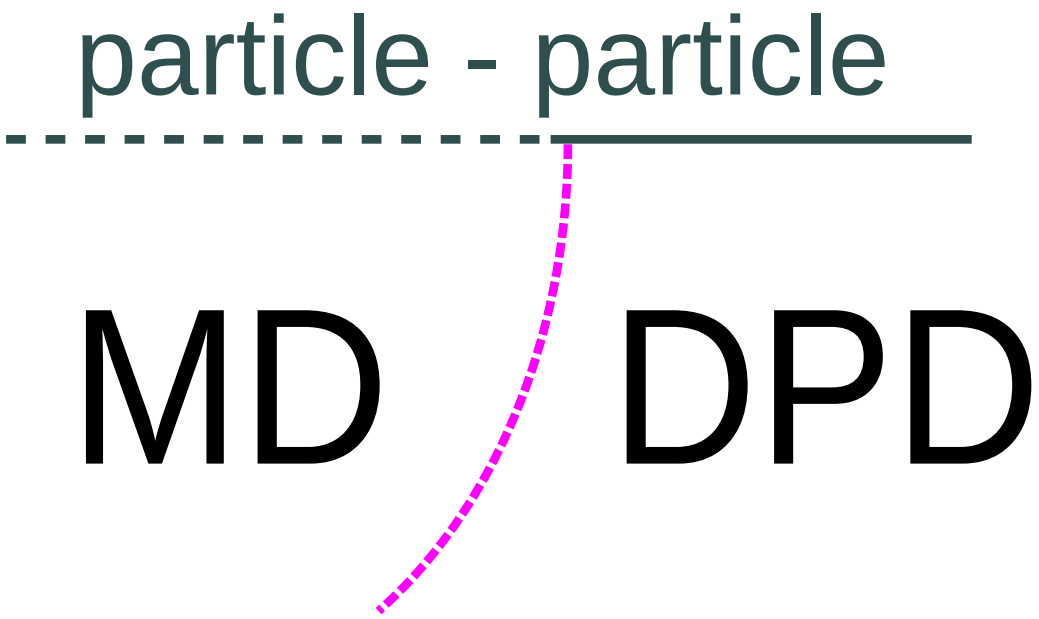
Dissipative particle dynamics

$$
\begin{aligned}
m_i \frac{d\mathbf{v}_i}{dt} &= \sum_{i \neq j} \mathbf{F^C}_{ij} + \mathbf{F^D}_{ij} + \mathbf{F^R}_{ij} \\
\mathbf{F^D}_{ij} dt &= -m_i \gamma \omega^2(r_{ij}) [\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij}] \hat{\mathbf{r}}_{ij} dt \\
\mathbf{F^R}_{ij} dt &= m_i \sigma \omega(r_{ij}) \hat{\mathbf{r}}_{ij} dW_{ij} \\
m\sigma^2 &= 2\gamma kT
\end{aligned}
\tag{1}
$$

Molecular dynamics

$$
m_i \frac{d\mathbf{v}_i}{dt} = \sum_{i \neq j} \mathbf{F^C}_{ij} + (\text{thermostats})
$$

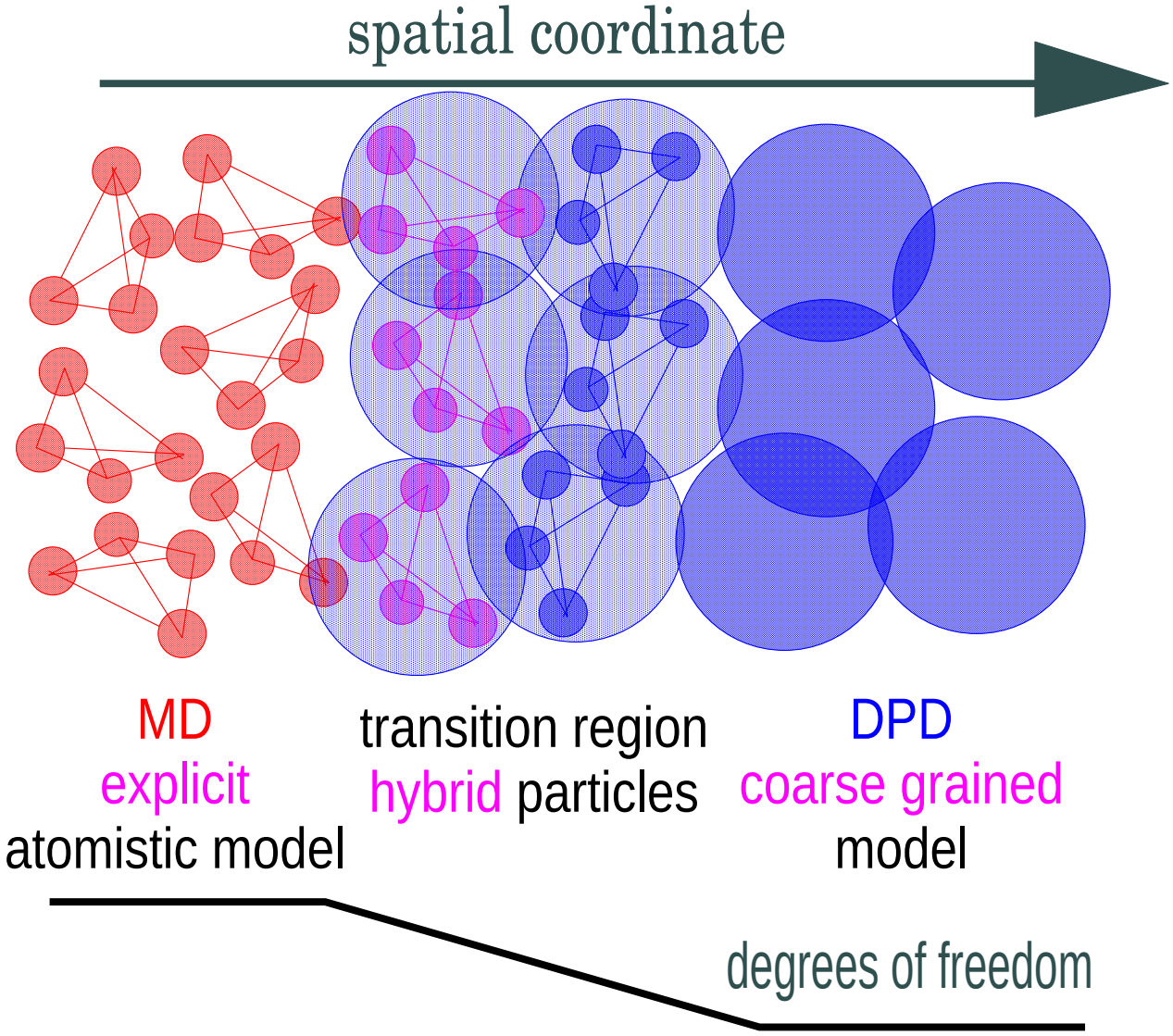
The essential difference lies in how steep the conservative forces are. **Coarse-grained molecular dynamics** is an intermediate step between soft (linear) forces and hard core repusions in atomistic MD.


particle - particle
MD
DPD

Coupling MD to DPD

Adaptive Resolution Scheme (AdResS)

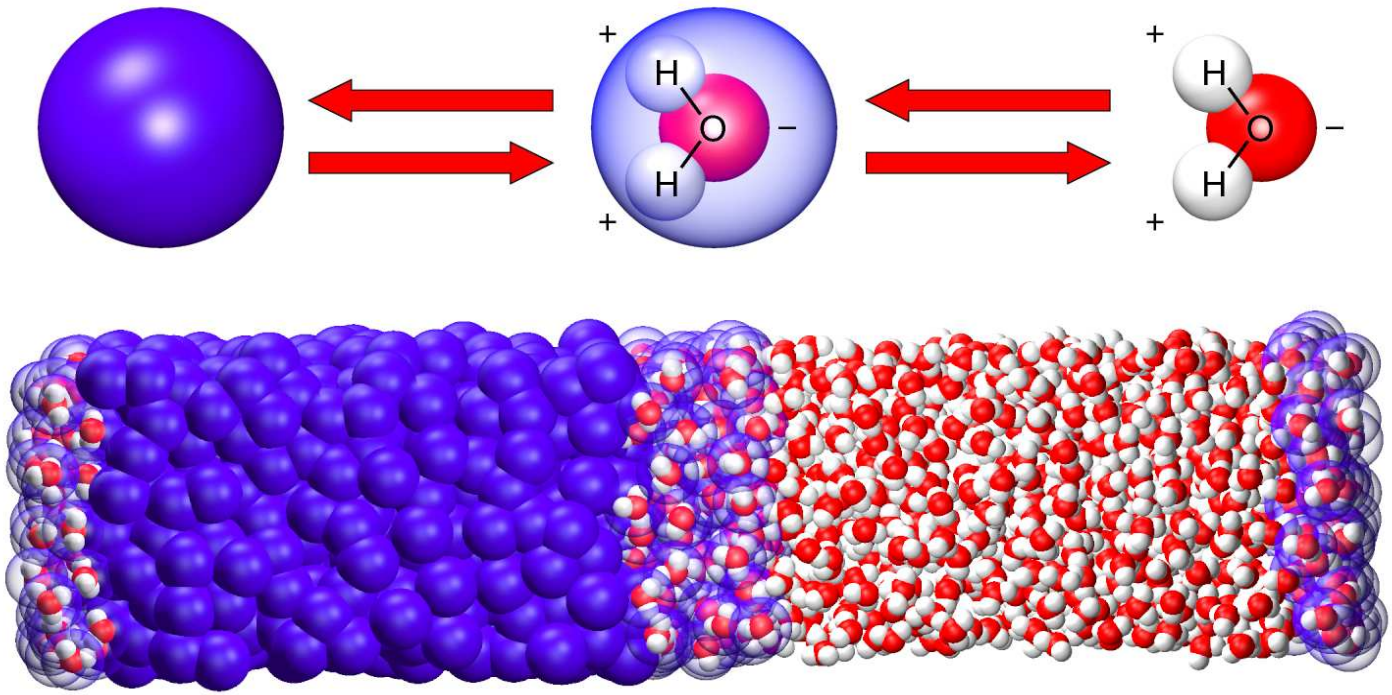
M. Praprotnik, L. DelleSite and K.Kremer, J. Chem.Phys **123** 224106 (2005), Ann. Rev. Phys. Chem. **59** 545 (2008)



Coupling MD to "DPD"

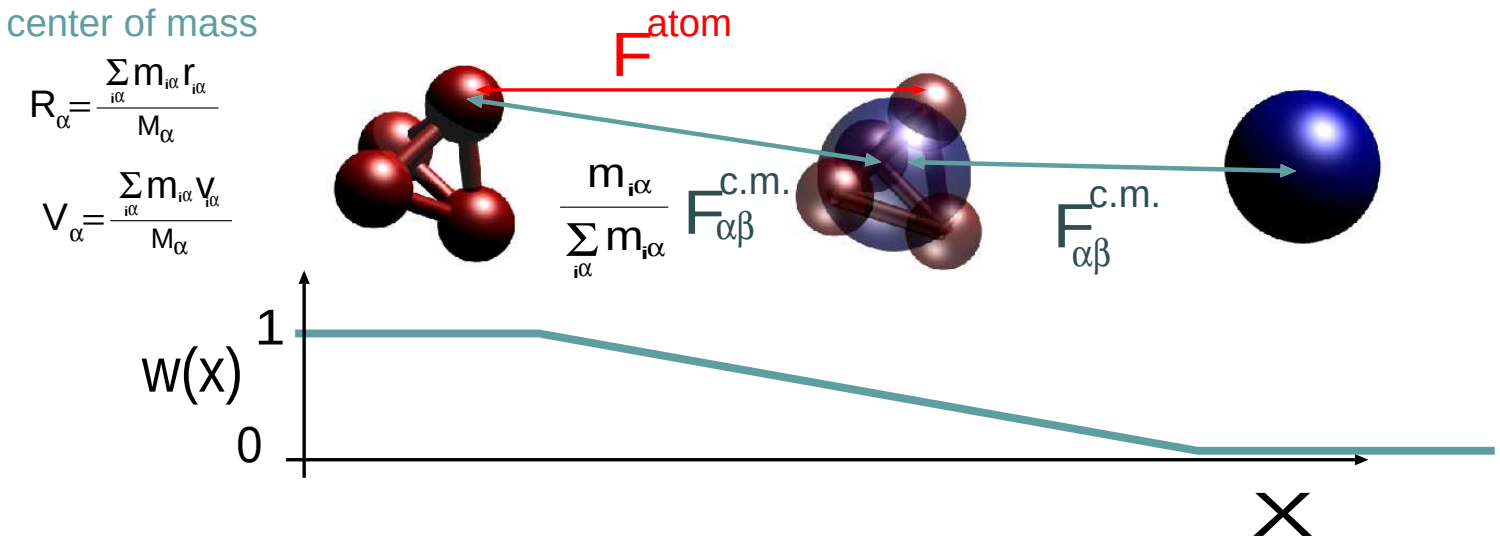
Adaptive Resolution Scheme for liquid water

M. Praprotnik, et a. J.Phys. Condens. Matter **19** (2007)



Coupling MD to "DPD"

Adaptive Resolution Scheme



$$\mathbf{F}_{\alpha\beta} = w(x_\alpha)w(x_\beta)\sum_{i\alpha j\beta}\mathbf{F}^{\rm atom}_{i\alpha j\beta} + [1 - w(x_\alpha)w(x_\beta)]\mathbf{F}^{\rm c.m.}_{\alpha\beta}$$

$$\mathbf{F}^{\rm atom}_{i\alpha j\beta} = -\frac{\partial U^{\rm atom}}{\partial \mathbf{r}_{i\alpha j\beta}} \quad \textbf{Atomistic}$$

$$\mathbf{F}^{\rm c.m.}_{\alpha\beta} = -\frac{\partial U^{\rm c.m.}}{\partial \mathbf{R}_{\alpha\beta}} \quad \textbf{Coarse – Grained}$$

(2)

Coupling MD to DPD

Effective potential for c.m. interaction

- The effective pair potential $U^{c.m.}$ is determined so as to match the center of mass radial distribution function of the *explicit* atomistic model, ${g^{ex}}_{cm}(r)$.

- This can be done using the `iterative Bolzmann inversion` [J. Comput. Chem. **24**1624 (2003)], which starts from the Potential of Mean Force as initial guess $(k = 0)$.

$$U^{cm}_{k+1}(r) = U^{cm}_{k}(r) + T \log \frac{g^{cg}_{k}(r)}{{g^{ex}}_{cm}(r)} \tag{3}$$

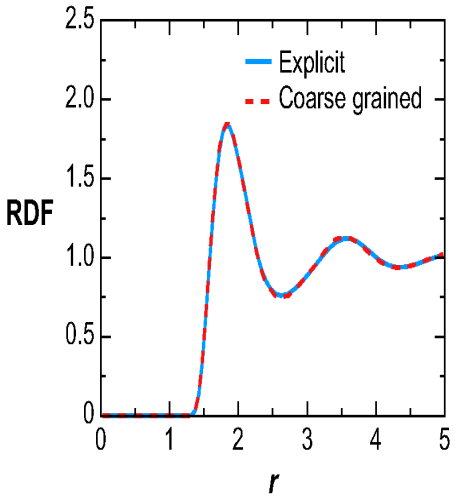
- Small correction $\Delta U^{cm} = U_0(1 - r/r_c)$ to equilibribrate pressures.

Coupling MD and DPD

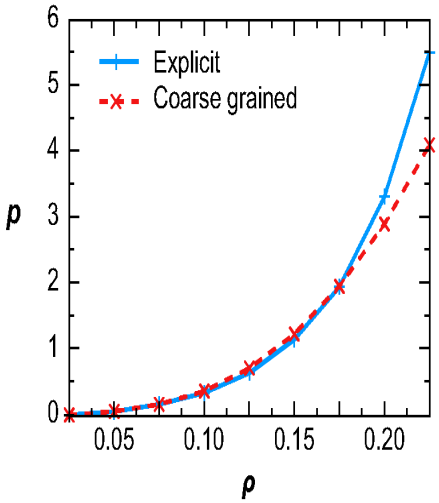
Matching liquid structure and pressure

Tetraedral fluid
kT = 1; ρ=0.175

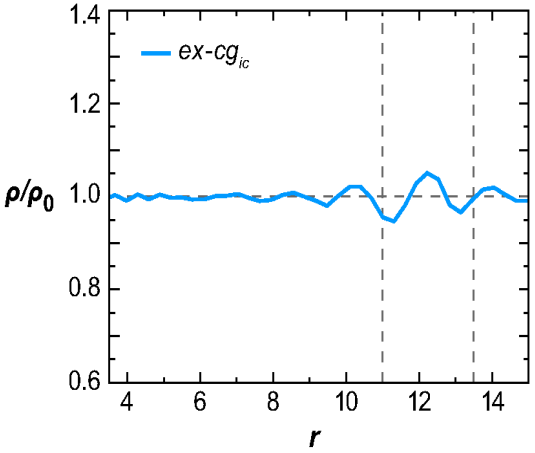
Radial distr. func.



pressure eos



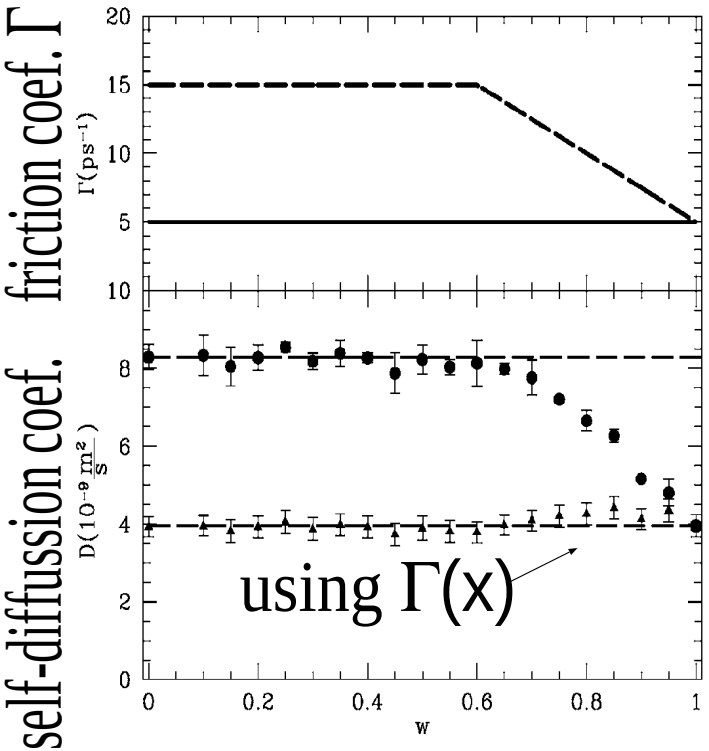
density profile



Coupling MD and DPD

Dynamics: self-diffusion across interfase

Position dependent Langevin thermostat



$$m_i \frac{dv_i}{dt} = F_i - m_i \Gamma(x_i) v_i + W_i(x_i, t)$$

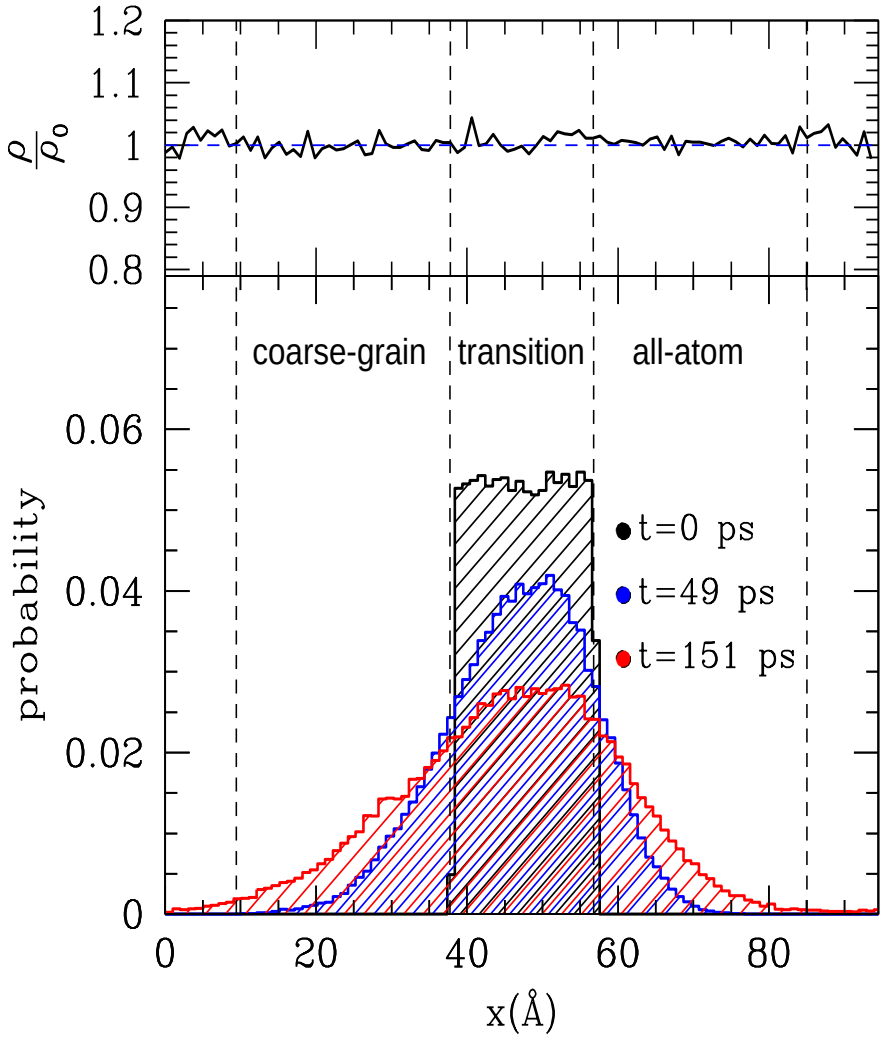
$$\langle W_i(x,0) \rangle = 0$$

$$\langle W_i(x,\tau) W_j(x,0) \rangle = 2\Gamma(x) kT \delta(\tau) \delta_{ij}$$

The thermostat at the "DPD" region is also needed to equilibrate the removed /added degrees of freedom (i.e. to add / remove the latent heat of transition).

Coupling MD and DPD

Dynamics: self-diffusion across interfase



Coupling MD and DPD

AdResS

`pros`

- Reduction of degrees of freedom for the liquid outside the region of interest.
- Conserves momentum (3rd Newton Law by construction)
- Recovers the fluid structure and pressure in the coarse-grained domain
- Self-diffusion of atomistic and coarse-grained domains can be *somehow* matched (a first-principles theory is lacking in the literature).

Coupling MD and DPD

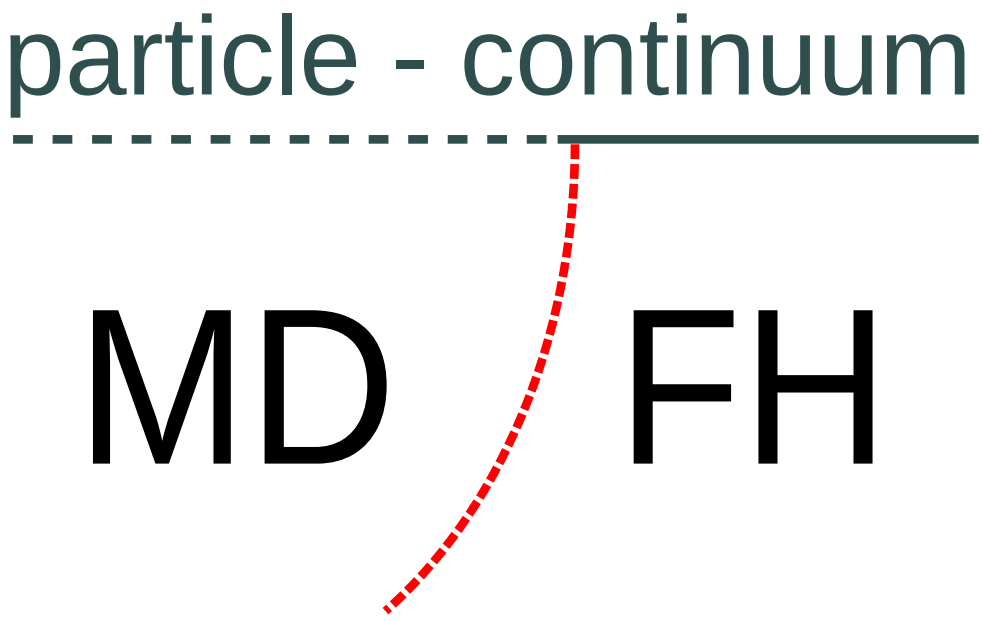
AdResS

`cons`

- It does not conserves energy $\Longrightarrow$ heat transfer is not described.

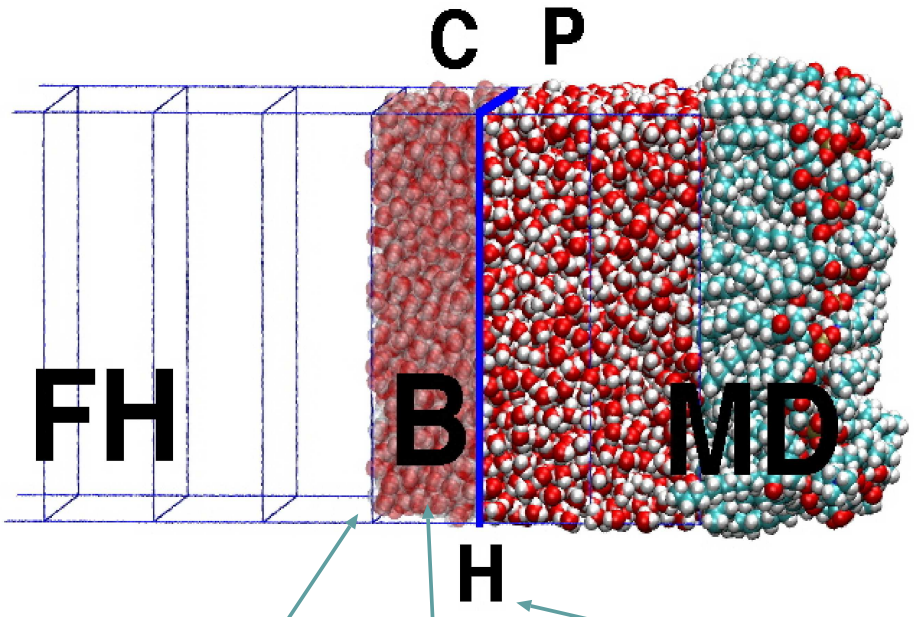
- Requires substantial pre-evaluation of the effective potential U^{cm} using `iterative Bolzmann inversion` for each fluid and thermodynamic state considered
  - Restricted to homogenous, or near equilibrium states
  - Pressure corrections using `iterative Bolzmann inversion` within the hybrid region might be required to obtain seamless density profiles.

- Viscosity mismatch between coarse-grained and atomistic models $\Longrightarrow$ incorrect shear transfer. This can be (partially) solved by using `transversal DPD` thermostat. C. Junghans et al., SoftMatter (2008).


particle - continuum
MD
FH

MD-CFD **Domain decomposition**

General issues concerning particle-continuum coupling



Information exchanged
variables / fluxes

Time dependence
Steady / Unsteady

Fluctuations
Deterministic CFD or
Fluctuating Hydrodynamics (**FH**)

End of particles box
open / closed

Particle buffer B
Maxwell daemons or
External forces

Continuity at interface H
- imposed to P / imposed to C
- continuity in fluctuations

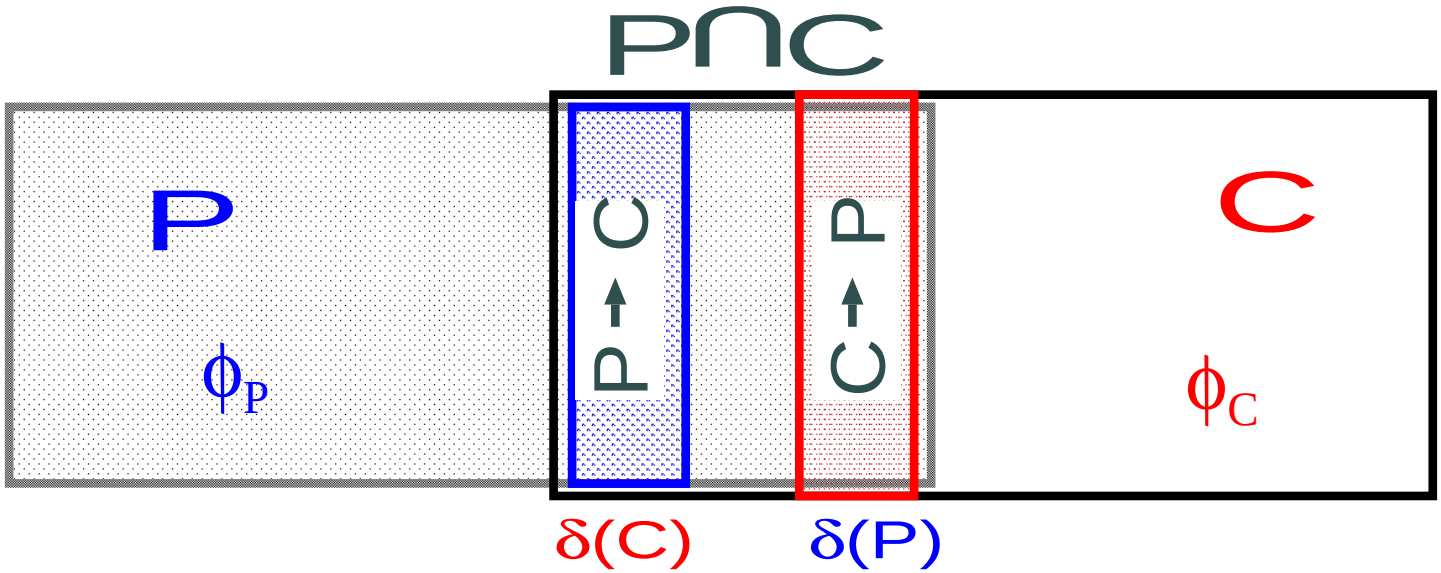
MD-CFD: **Hybrid schemes depending upon the exchanged information**

- **Coupling through variables:**
  - **Schwartz scheme**: steady state, closed system (only shear), no fluctuations.
  - **Constraint particle dynamics** (velocity imposition): unsteady, closed (only shear), no fluctuations.

- **Coupling through fluxes** (of momentum and energy)
  - **Unsteady** flows
  - **Open** molecular dynamics: **grand canonical ensemble**, generalized ensembles for MD.
  - Shear, **sound and heat** transfers (avoid finite size effect)
  - **Fluctuations** included (MD-Fluctuating hydrodynamics)

MD-CFD The Schwartz method

REFS: Hadjiconstantinou, Koumoutsakos



0) Solve C using an initial guess for ϕ_C at δ(C)

loop

1) Solve P imposing ϕ_C at δ(P) Maxwell Daemon for velocity

2) Solve C imposing $\langle\phi_P\rangle$ at δ(C) Dirichlet B.C.

Check for convergence within PNC

Constrained dynamics .vs. velocity continuity

	C imposes to P	P imposes to C
Authors	Nie *et al* (MD-CFD)	RDB (MD-FH); Garcia (DSMC-CFD)
velocity	Contrained particle dynamics	Relaxation BC for C
mass flux	Imposed to P	Measured from P

Constrained particle dynamics: Thompson and O'Connel, PRE, (1995); Nie *et al.* J. Fluid Mech. (2004)

$$\frac{dx_i^2}{dt} = F_i/m + \frac{1}{\tau_r}\left(v_B^C - \langle v \rangle_B^P\right)$$

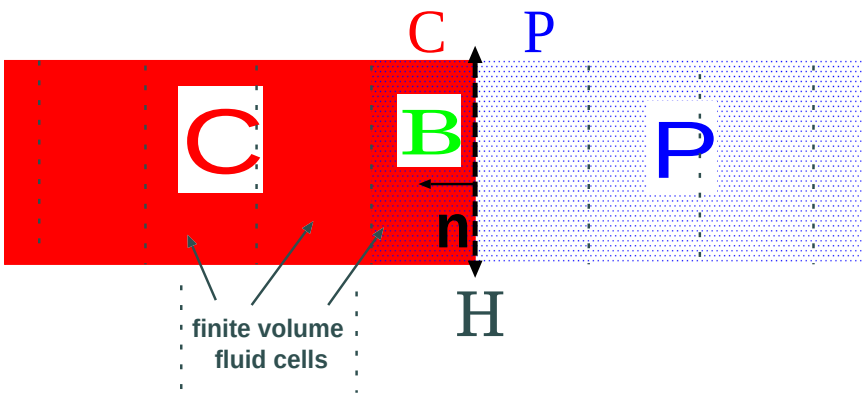
Continuum velocity relaxation: RDB, Flekkoy, P.Coveney, EuroPhys. Lett. (2005)

$$\frac{[\Delta\rho\mathbf{v}]_H^C}{\Delta t} = [\mathrm{Navier-Stokes}] + \frac{1}{\tau_r}\left(\langle [\rho\mathbf{v}]^P \rangle_H - [\rho\mathbf{v}]_H^C\right)$$

Note: Constraining the particle dynamics affects the particle collective properties. It also destroys energy balance. Relaxation of C is simple and efficient, $\tau_r << \tau_{hydro}$.

MD-CFD **Flux exchange**

REFS: E. Flekkoy EPL (2000); A. Garcia (AMAR)m J.Comp.Phys (1999); Delgado-Buscalioni (HybridMD), PRE (2002), PRL (2007).



Continuum sudomain: C
Particle subdomain: P
Particle buffer: B

Total system : C+P
Extended system: C+P+B

Flux of ϕ across hybrid interface H

$$J_\phi^H = \frac{\left(J_\phi^{PC} + J_\phi^{CP}\right)}{2}$$

Conservation

$$\Delta\phi_C = A\, J_\phi^H . \mathbf{n}\, \Delta t$$

$$\Delta\phi_P = -A\, J_\phi^H . \mathbf{n}\, \Delta t$$

Conservation laws apply for the total system: P+C

G. De Fabritiis, RDB, P. Coveney; PRL 97, 134501 (2006)
RDB, G. De Fabritiis; PRE 76, 036709 (2007)

Continuum fluid dynamics

- **Conservation law** conserved quantity per unit volume Φ

$$\partial\Phi/\partial t = -\boldsymbol{\nabla}\cdot\mathbf{J}^{\phi}$$

mass	$\Phi = \rho$	$\mathbf{J}^{\rho} = \rho\mathbf{u}$
momentum	$\Phi = \boldsymbol{g} \equiv \rho\mathbf{u}(\mathbf{r},\mathbf{t})$	$\mathbf{J}^{\boldsymbol{g}} = \rho\mathbf{u}\mathbf{u} + \boldsymbol{P}$
energy	ρe	$\mathbf{J}^{e} = \rho\mathbf{u}e + \boldsymbol{P}:\mathbf{u} + \boldsymbol{Q}$

- **Closure relations**

Equation of state $p = p(\rho)$

Constitutive relations

Pressure tensor $\boldsymbol{P} = p\mathbf{1} + \Pi + \tilde{\Pi}$

Viscous tensor $\Pi = -\eta\left(\nabla\boldsymbol{u} + \nabla\boldsymbol{u}^{T}\right) + (2\eta/3 - \xi)\,\nabla\cdot\boldsymbol{u}$

Conduction heat flux $\boldsymbol{Q} = -\kappa\nabla T + \tilde{Q}$

Fluctuating heat and stress a *la Landau*

Stress fluctuations $\langle\tilde{\Pi}(\boldsymbol{r}_1,t)\tilde{\Pi}(\boldsymbol{r}_2,0)\rangle = 2k_BTC_{\alpha\beta\gamma\delta}\delta(\boldsymbol{r}_2-\boldsymbol{r}_1)\delta(t)$

$C_{\alpha\beta\gamma\delta} = \left[\eta(\delta_{\alpha\delta}\delta_{\beta\gamma} + \delta_{\alpha\gamma}\delta_{\beta\delta} + (\zeta - \tfrac{2}{3}\eta)\delta_{\alpha\beta}\delta_{\delta\gamma}\right]$

Heat flux fluctuations $\tilde{Q}$

The finite volume scheme

Finite volume schemes for fluctuating hydrodynamics

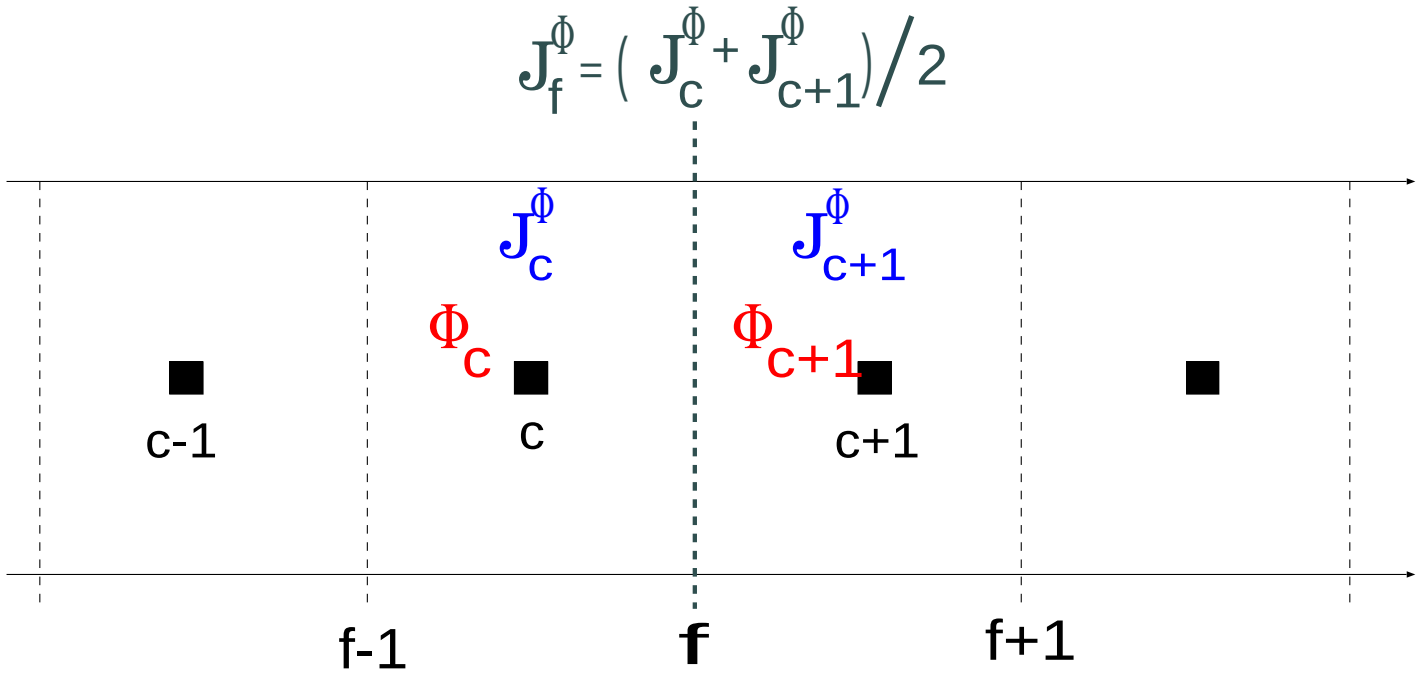
- FH for argon and water: G. De Fabritiis et al PRE, **75** 026307 (2007)
- Open BC for FH: RDB and A. Dejoan, PRE (accepted)
- Staggered grid for FH: RDB and A. Dejoan, (preprint)

$$\int_{V_c} \partial\Phi/\partial t = -\oint_{S_\alpha} \mathbf{J}^\phi \cdot \boldsymbol{ds}$$

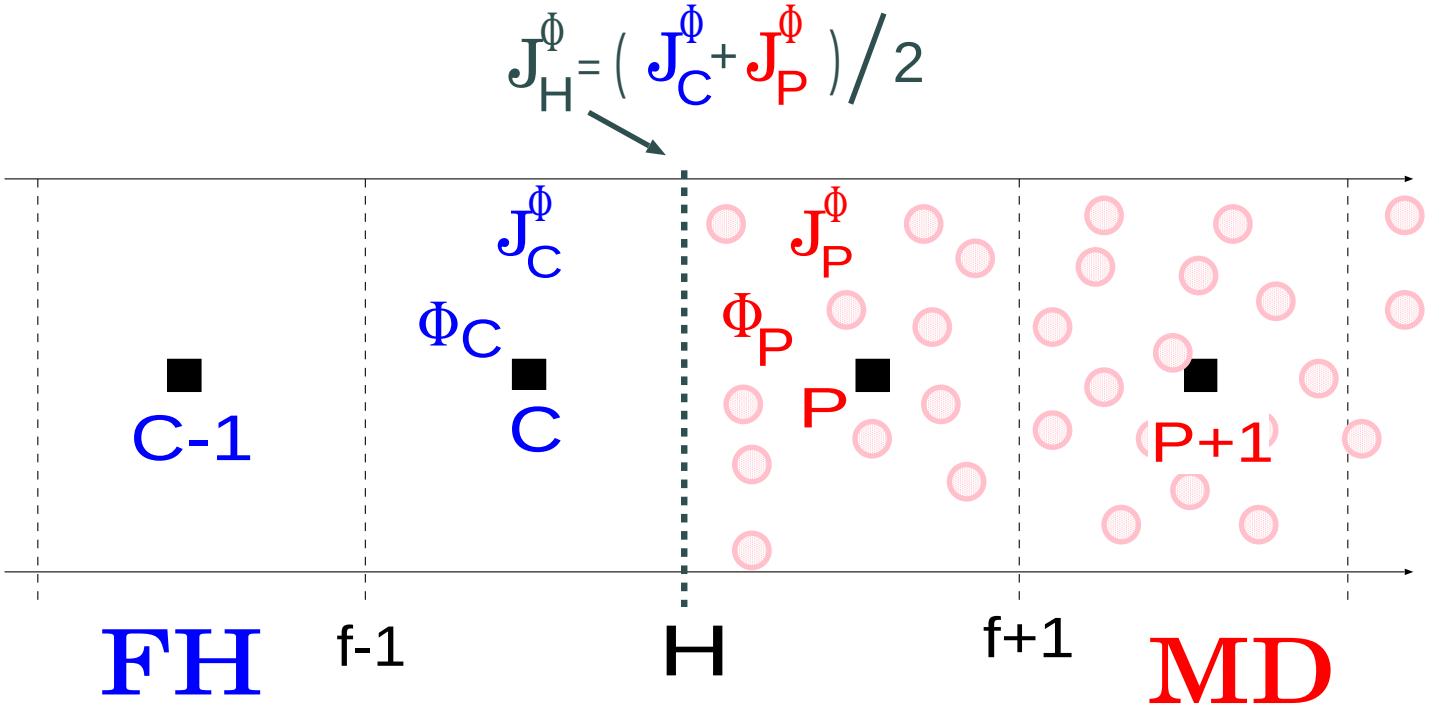
$$V_c \frac{\Delta\Phi_c}{\Delta t} = -\sum_{f=\text{faces}} A_f \mathbf{J}_f^\phi \cdot \boldsymbol{e}_f \quad \text{(explicit Euler scheme)}$$

mass	$\Phi = \rho$	$\mathbf{J}^\rho = \rho\mathbf{u}$
momentum	$\Phi = \boldsymbol{g} \equiv \rho\mathbf{u}(\mathbf{r},\mathbf{t})$	$\mathbf{J}^{\boldsymbol{g}} = \rho\mathbf{u}\mathbf{u} + \boldsymbol{P}$
energy	ρe	$\mathbf{J}^e = \rho\mathbf{u}e + \boldsymbol{P} : \mathbf{u} + \boldsymbol{Q}$

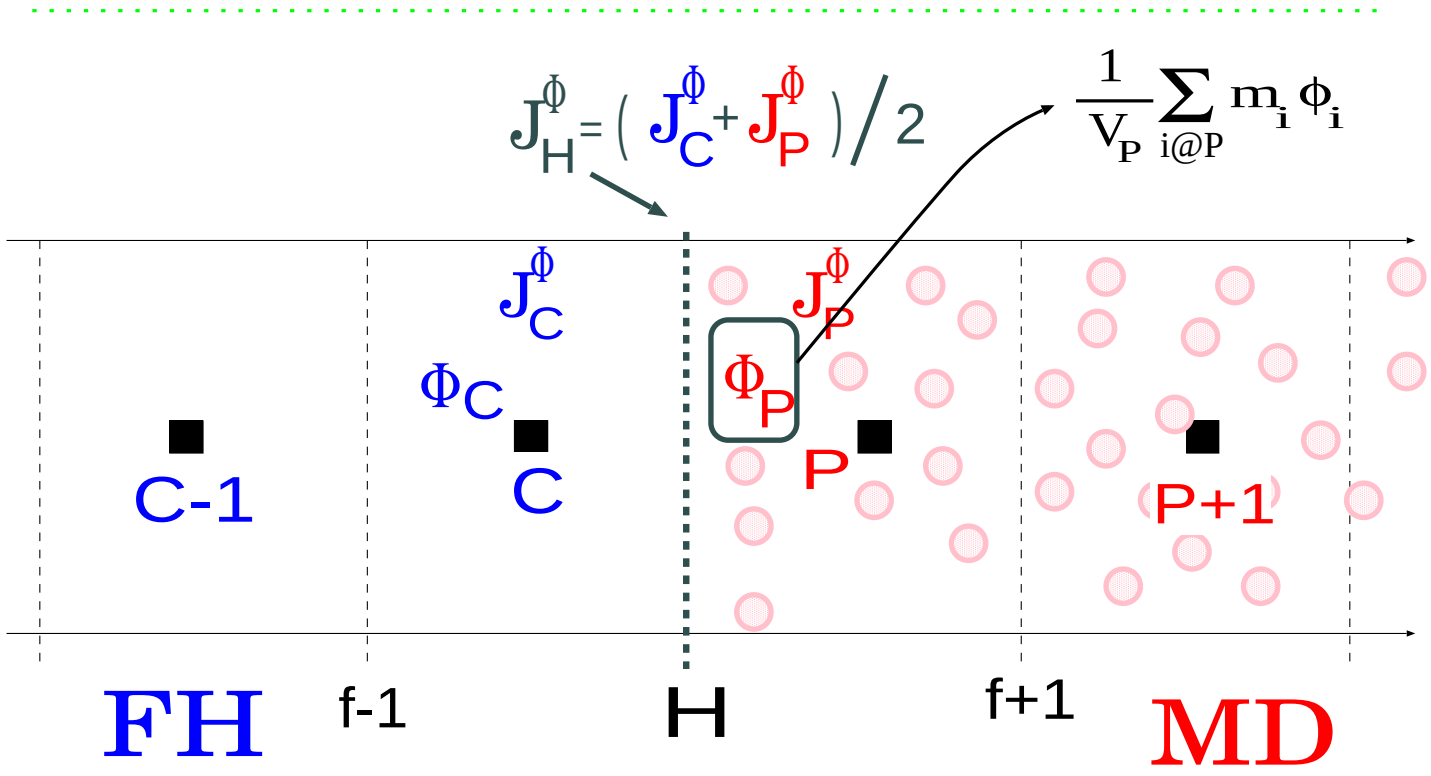
Finite volume scheme



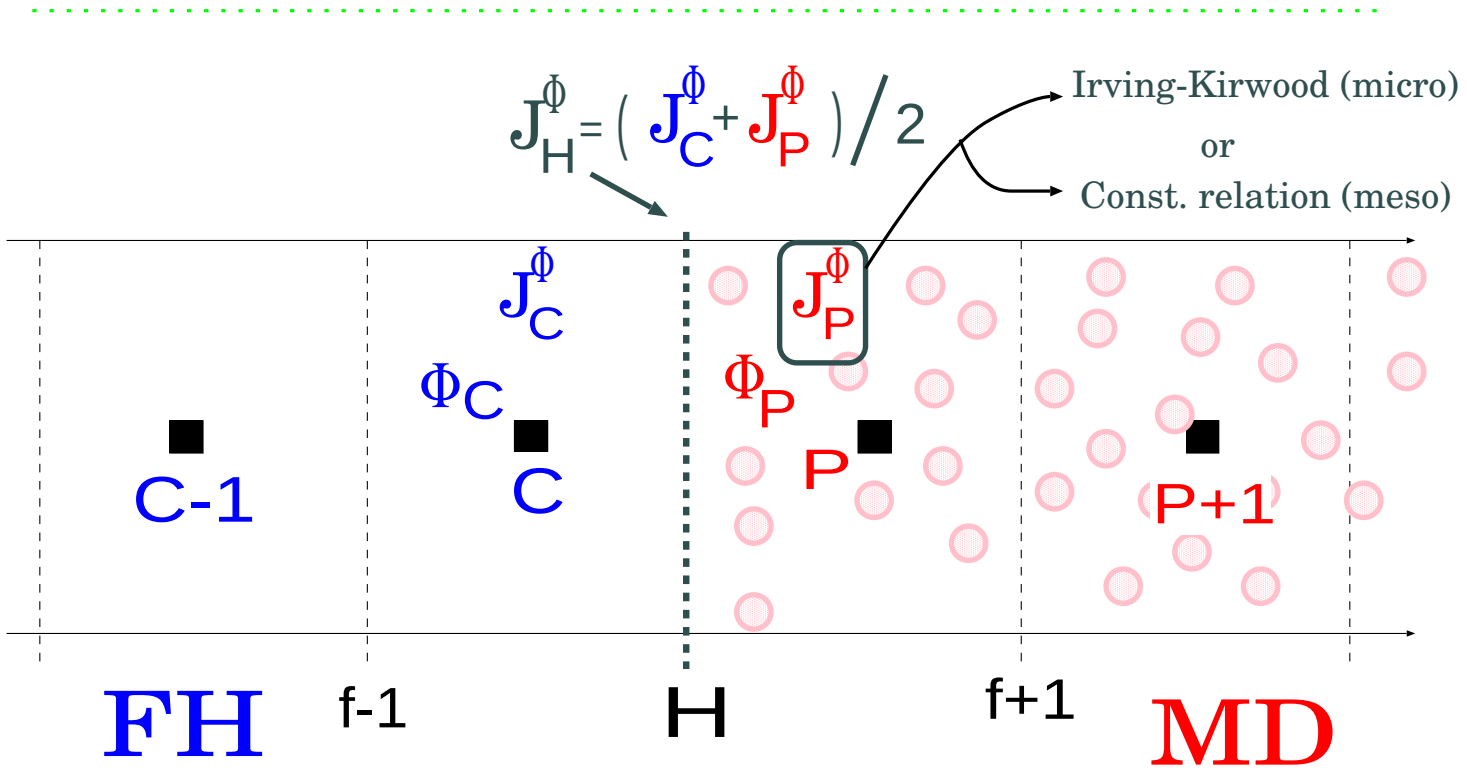
MD-FH: **hybridMD scheme**



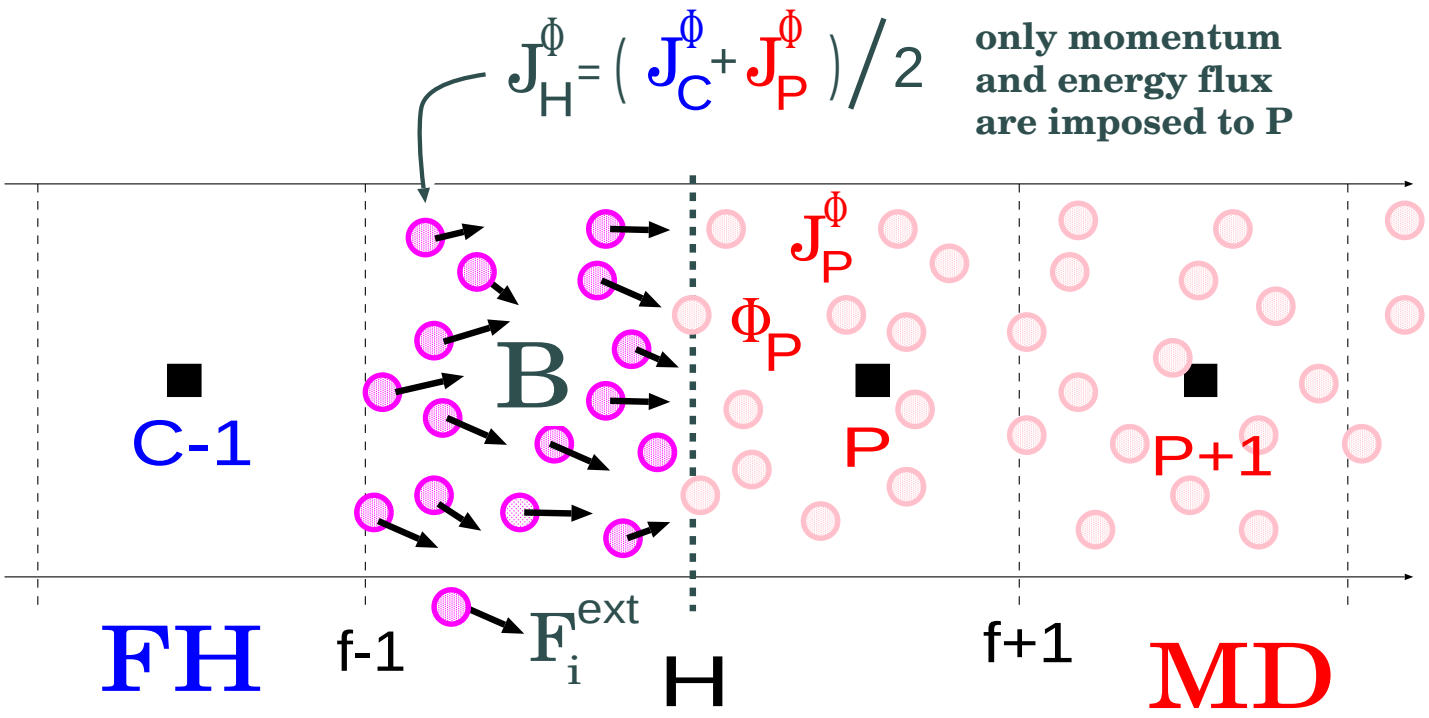
MD-FH: **Local P variables**



MD-FH: **Local P fluxes**

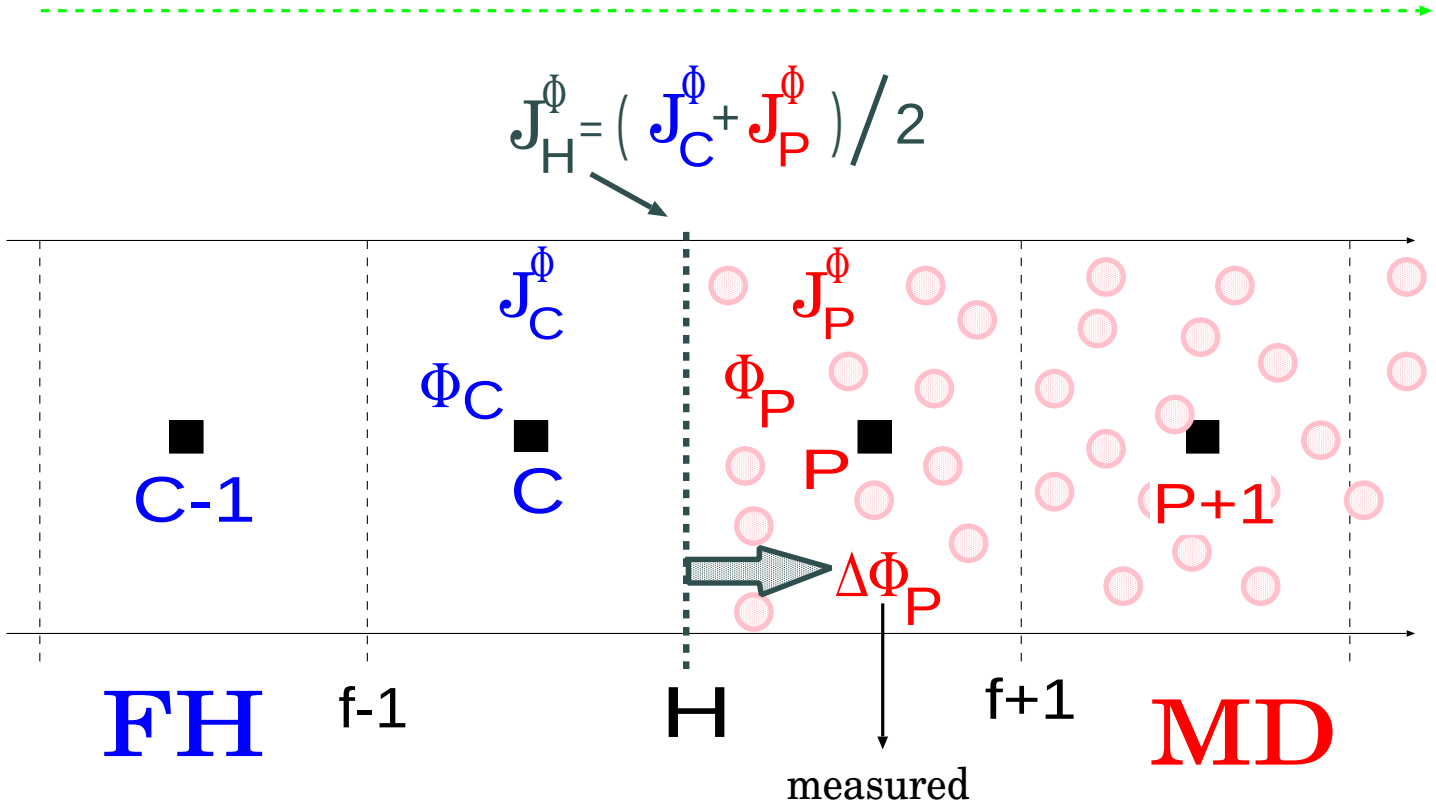


MD-FH: **Imposing fluxes into MD**

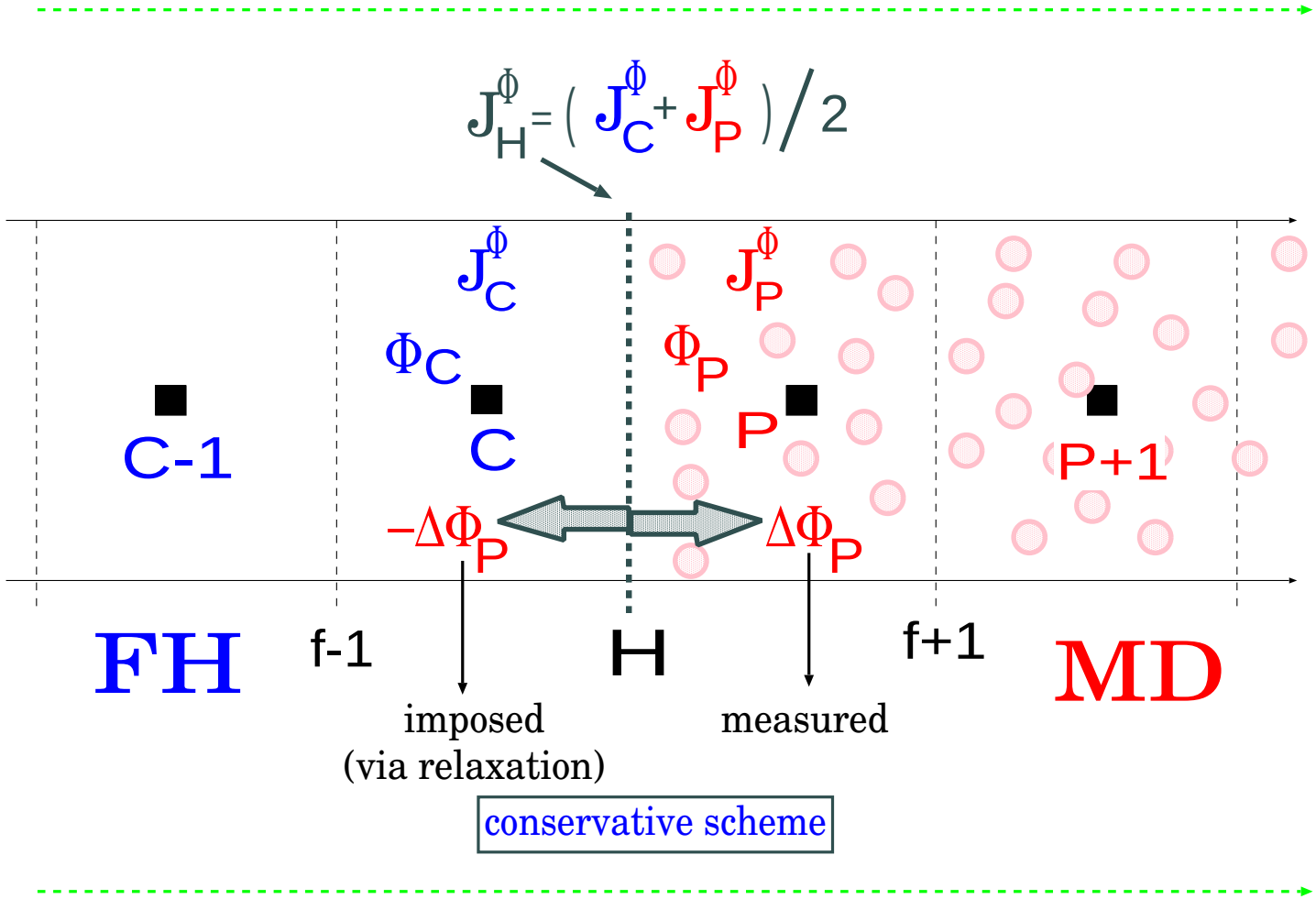


flux correction

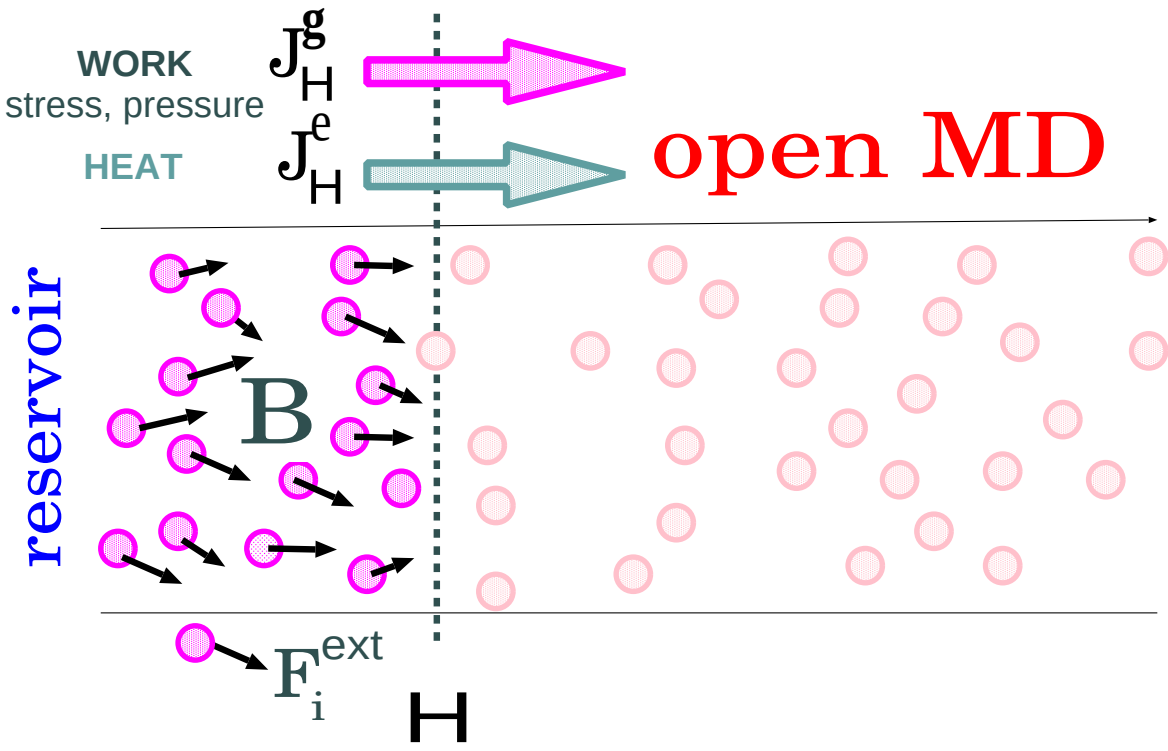
MD-FH: **flux balance**



MD-FH: **flux balance: conservative scheme**



open molecular dynamics



MD-FH **Flux boundary conditions for** `open MD`

Flekkoy, RDB, Coveney, PRE **72**, 026703 (2005)

Energy flux J_e and momentum flux $\mathbf{J_p}$ imposed into MD across H

$$\begin{array}{lrcll} \text{Momentum over } \Delta t & \mathbf{J_p} A \Delta t & = & \sum_{i\in B} \mathbf{F}_i^{ext} \Delta t & + \quad \sum_{i'} \Delta(m\mathbf{v}_{i'}) \\ \text{Energy over } \Delta t & \underbrace{J_e A \Delta t}_{\text{Total input}} & = & \underbrace{\sum_{i\in B} \mathbf{F}_i^{ext} \cdot \mathbf{v}_i \Delta t}_{\text{External force}} & + \quad \underbrace{\sum_{i'} \Delta\epsilon_{i'}}_{\text{Particle insertion/removal}} \end{array}$$

External forces: $\mathbf{F}_i^{ext} = \langle \mathbf{F}_i^{ext} \rangle + \tilde{\mathbf{F}}_i^{ext}$ (particle $i \in B$)

Momentum: introduced by the mean external force $\langle \boldsymbol{F}_i \rangle$

$$\langle \mathbf{F}^{ext} \rangle = \frac{A}{N_B} \tilde{\mathbf{j}}_p \quad \text{where } \tilde{\mathbf{j}}_p \equiv \mathbf{J_p} - \frac{\sum_{i'} \Delta(m\mathbf{v}_{i'})}{A\, dt} \, .$$

Energy: introduced by the fluctuating force $\tilde{\mathbf{F}}_i^{ext}$ via dissipative work.

$$\tilde{\mathbf{F}}_i^{ext} = \frac{A\mathbf{v}_i'}{\sum_{i=1}^{N_B} \mathbf{v}_i'^2} \left[\tilde{j}_e - \tilde{\mathbf{j}}_p \cdot \langle \mathbf{v} \rangle \right] \qquad \text{with } \tilde{j}_e \equiv J_e - \frac{\sum_{i'} \Delta\epsilon_{i'}}{Adt}.$$

Molecular dynamics at various ensembles

Flekkoy, RDB, Coveney, PRE, **72**, 026703 (2005)

- THE AMOUNT OF HEAT AND WORK INTO THE MD SYSTEM IS EXACTLY CONTROLLED

- The system comunicates with the exterior at its boundaries (B), as a real system does.

- Grand-canonical ensemble. μVT, with $\mu = \mu(p^C, T^C)$ chemical potential at the reservoir B. **Dynamics of confined systems**

- Isobaric ensemble NPT. $\mathbf{J_p} = p\hat{\mathbf{n}}$.

- Constant enthalpy HPT. $\mathbf{J}_e^H = M\langle \mathbf{v} \rangle \cdot F$ and $\Delta N = 0$. $\Delta E + p\Delta V = \Delta H = 0$. (Joule-Thompson), **MD-calorimeter**

- Constant heat flux. $\mathbf{J}_e = cte$. (**melting dynamics**, growth of solid phase -ice-, heat exchange at complex surfaces...)

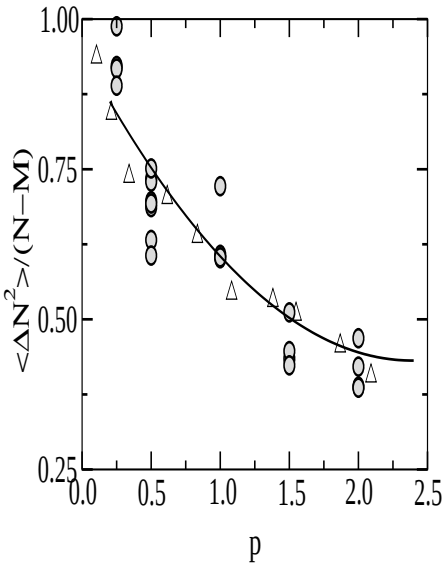
Mass fluctuations: grand canonical ensemble

$$\texttt{Var}[\rho] = k_B T \rho / (V c_T^2) \text{ with } c_T^2 = (\partial p / \partial \rho)_T$$

Flux particle BC´s are thermodynamically consistent

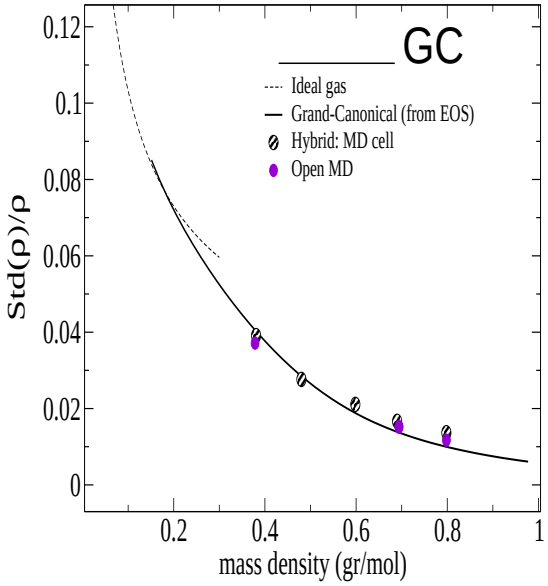
with the Grand Canonical ensemble

Soft-particles
DPD-like



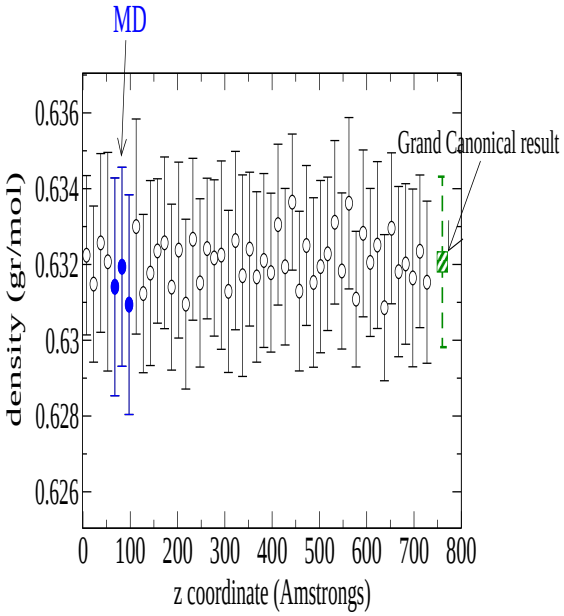
pressure

Liquid argon



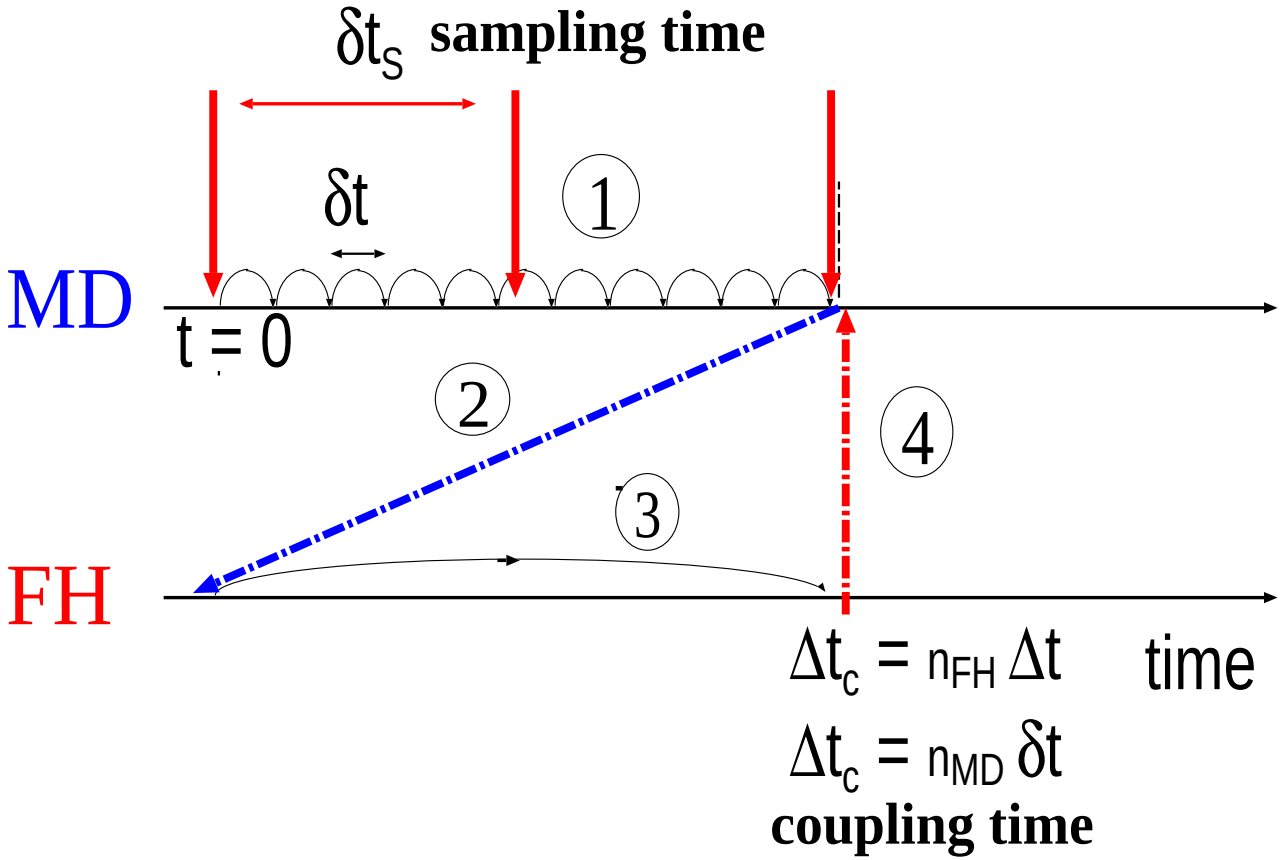
density

Water (T=300 K)



cell-coordinate

MD-FH Time coupling



MD-FH Coupling time and stress fluctuations

Green-Kubo relations

- Molecular dynamics: decorrelation time $\tau_c \sim 100$fs (simple liquids)

$$\langle J^2_{MD} \rangle = \frac{\eta k_B T}{V \tau_c} \text{ with, } \tau_c \equiv \frac{\int_0^\infty \langle J(t) J(0) \rangle dt}{\langle J(0)^2 \rangle}$$

- Fluctuating hydrodynamics: decorrelation time $\Delta t/2$,

$$\langle J^2_{FH} \rangle = \frac{2\eta k_B T}{V \Delta t}$$

Thus for $\boxed{\langle J^2_{MD} \rangle = \langle J^2_{FH} \rangle}$ the decorrelation times should coincide:

$$\Delta t = 2\tau_c = \delta t_S \;\; \text{Smallest coupling time} = \text{Sampling time}$$

In general,

$$\boxed{\Delta t_c = n_{FH} \Delta t = 2 N_s \tau_c}$$

The buffer's tasks

- **Distribute external forces** to impose momentum and energy in MD

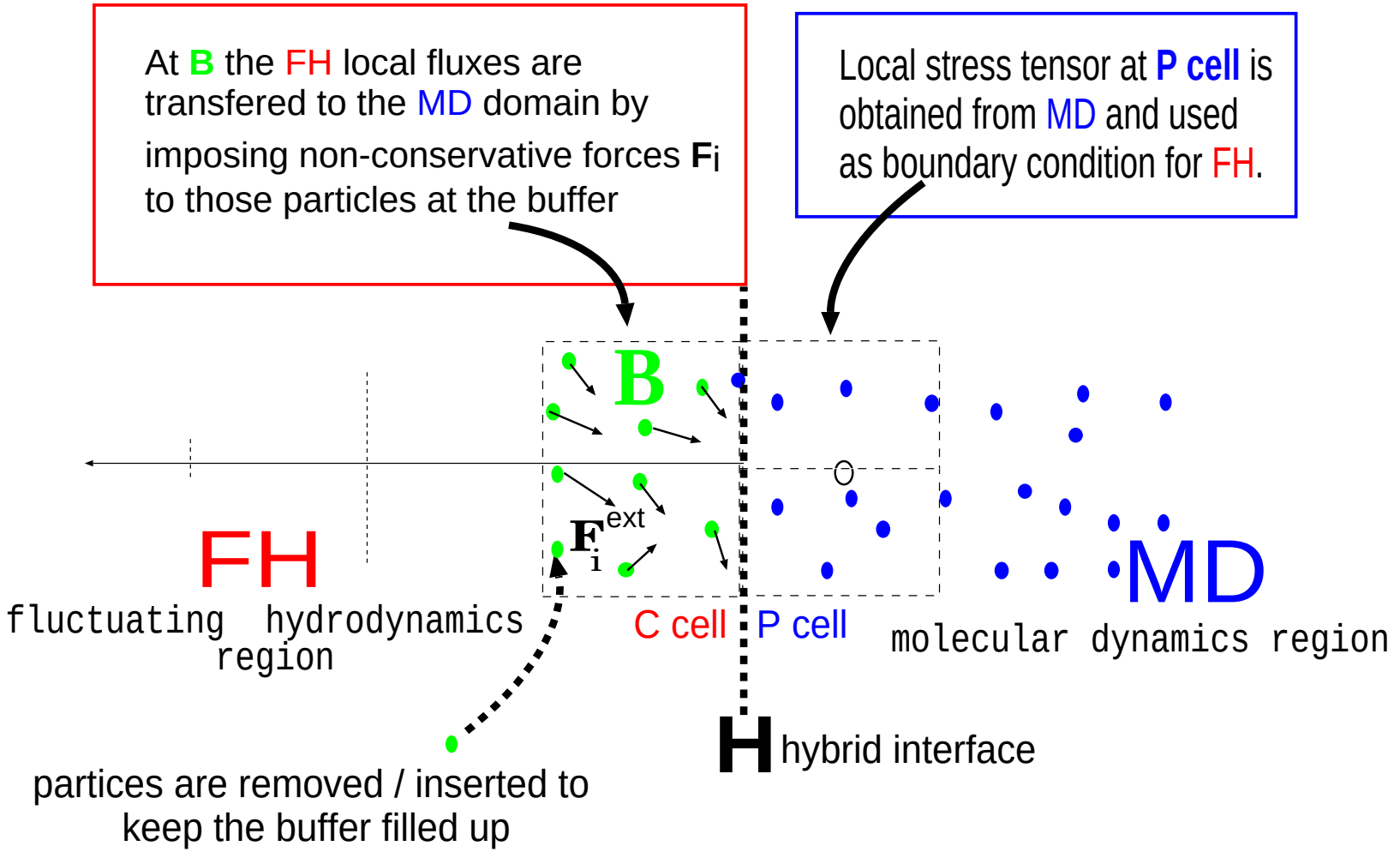
- **Mass reservoir**: mean buffer mass $\langle M_B \rangle = m \langle N_B \rangle$ controlled by a simple relaxation algorithm:

$$\frac{dN_B}{dt} = \frac{1}{\tau_B} (\alpha N_C - N_B)$$

with $\tau_B \simeq [10 - 100] fs$ (faster than any hydrodynamic time) and $\alpha \simeq 0.75$.

- **Open system:**
  - Particles leaving the buffer end are removed
  - Particle insertion ($\Delta N_B > 0$) using the USHER algorithm [J. Chem. Phys, **119**, 978 (2003)]

MD-CFD **Flux imposed at the particle buffer B**

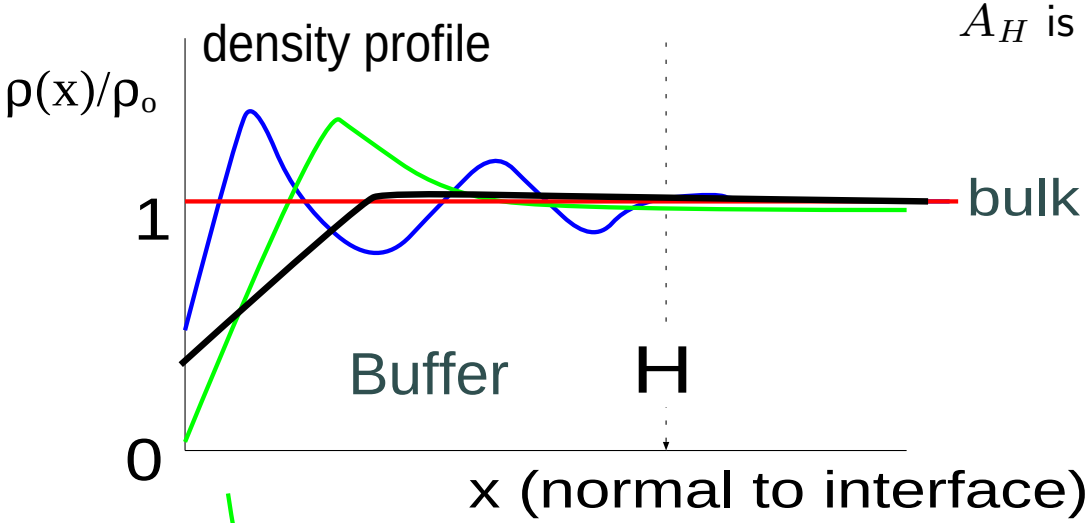


particle insertions using the **USHER** method:
LJ insertion: J. Chem. Phys., 119, 978 (2003)
water insertion: J.Chem.Phys.121, 12139 (2004)

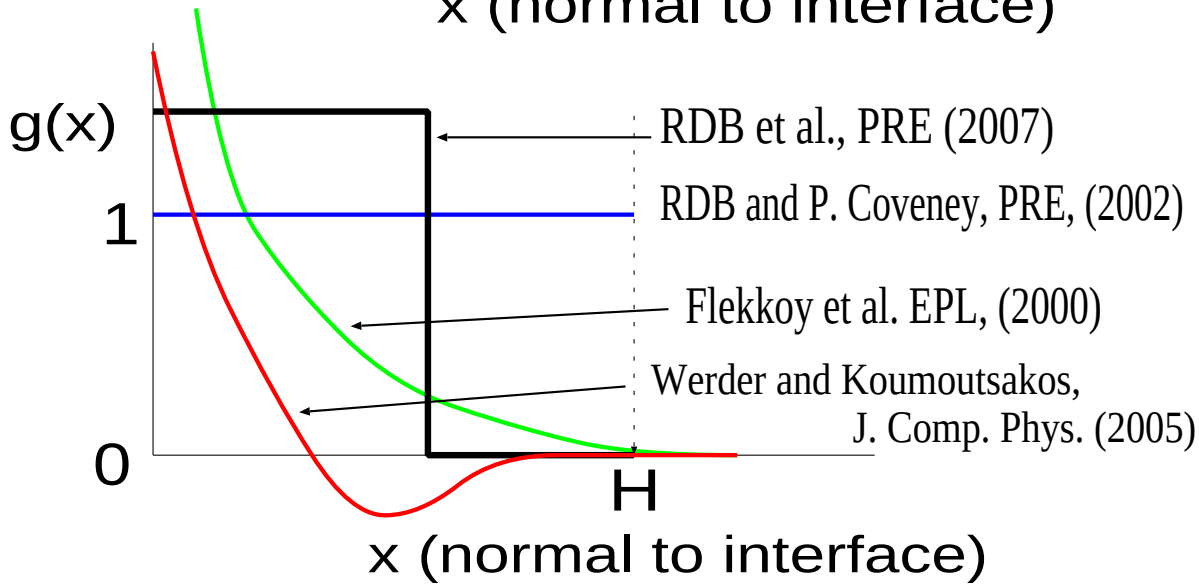
MD-CFD **Force distribution at the buffer**

Momentum flux across H: $\mathbf{J}_H \cdot \mathbf{e}_H$

A_H is the area of the interfase H



$$F_i^{ext} = \frac{g(x_i)}{\sum_{i \in B} g(x_i)} A_H \mathbf{J}_H \cdot \mathbf{e}_H$$



USHER energy controlled molecule insertion

J. Chem. Phys **119**, 978 (2003); J. Chem. Phys. **121**, 12139 (2004) (water)

- **Objective**: Insert a new molecule at target potential energy E_T.
- **Method**: Newton-Raphson-like search in the potential energy landscape.
  Succesful insertion $|\Delta E/E_T| < 0.01$ where $\Delta E = E_T - E_i^{(n)}$

Translation of the centre of mass along force direction $\boldsymbol{F}$

$$\mathbf{r}_{cm}^{n+1} = \mathbf{r}_{cm}^{n} + \frac{\mathbf{F}_{cm}^{n}}{F_{cm}^{n}}\delta r$$

Rotation around the torque axis: (water)

$$\mathbf{r}_{cm,i}^{n+1} = \mathcal{R}_{\delta\theta}^{(n)}\mathbf{r}_{cm,i}^{n}$$

$\delta r = \min(\Delta E/F, \Delta R_{\max})$;
$\Delta R_{\max} \simeq$ half distance of first peak of radial distribution
$\delta\theta = \min(\Delta E/\tau, \Delta\Theta_{\max})$
the maximum rotation allowed is $\Delta\Theta_{\max} \sim 45^o$

Thermodynamically controllable process: Local ENERGY, TEMPERATURE and PRESSURE and are kept at the proper equation of state values.

Negligible insertion cost:

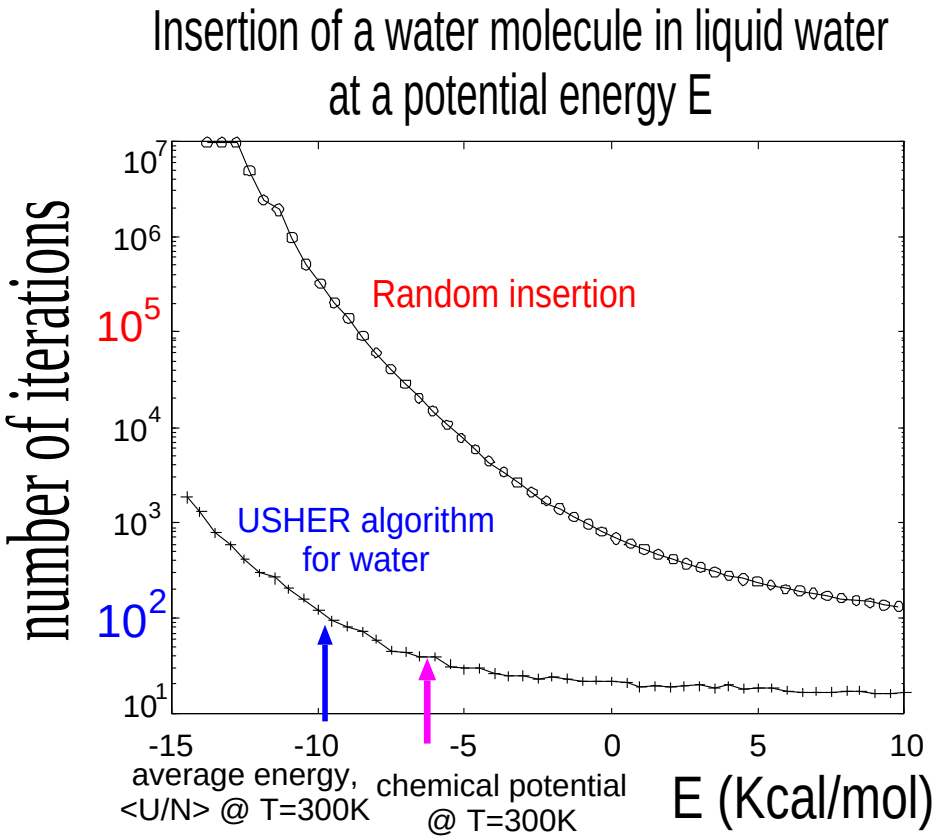
LJ particles ($\rho < 0.85$)	$< 1\%$ total CPU
Water into water	$\sim 3\%$ total CPU

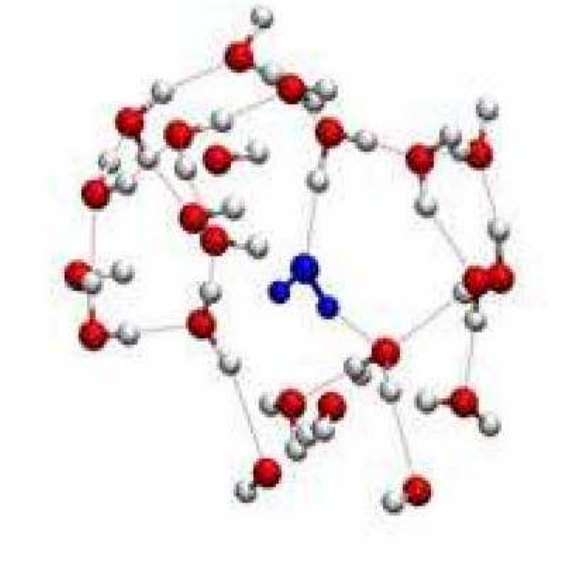
Insertions done at the mean energy/molecule contribution $E_T = 2U_{eos}$

USHER: fast and controlled particle insertion

J. Chem. Phys **119**, 978 (2003); J. Chem. Phys. **121**, 12139 (2004) (water)

Applications: Constant chemical potential simulations, unfolding of proteins via water insertion (Goodfellow), water insertion in confined systems (e.g. proteins).

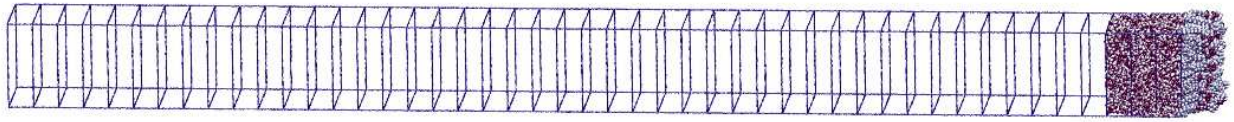




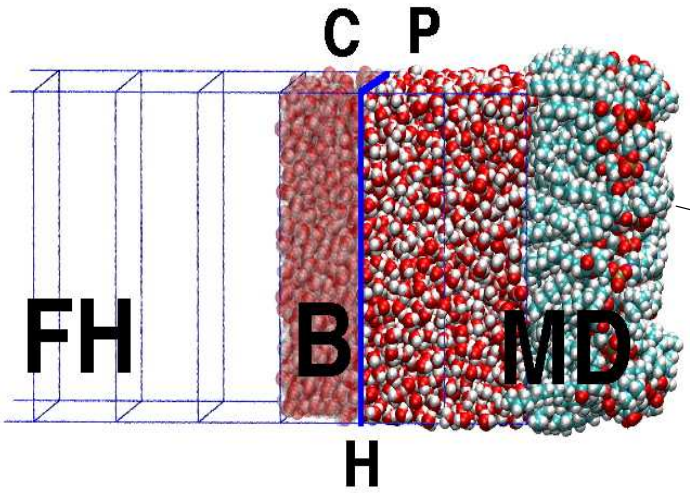
MD-FH Setup for tests

Water against a lipid layer at $T = 300K$
[G.Fabritiis,RDB, Coveney PRL, **97** (2006)].

Multiscale modelling
Embedding molecular dynamics within fluctuating hydrodynamics

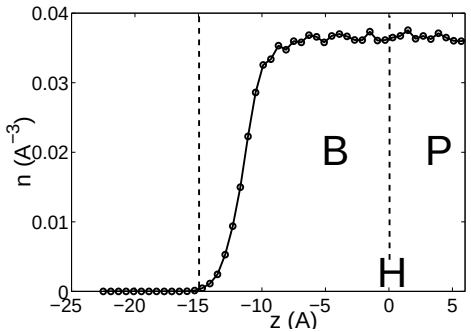


Hybrid MD-FH setup



DMPC
(lipid layer)

water density profile



PRL, 97, 134501 (2006)

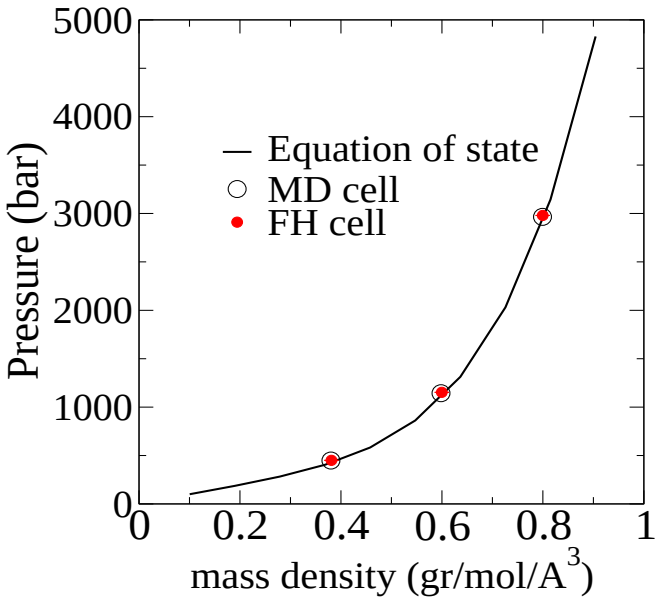
PRE, 76, 036709 (2007)

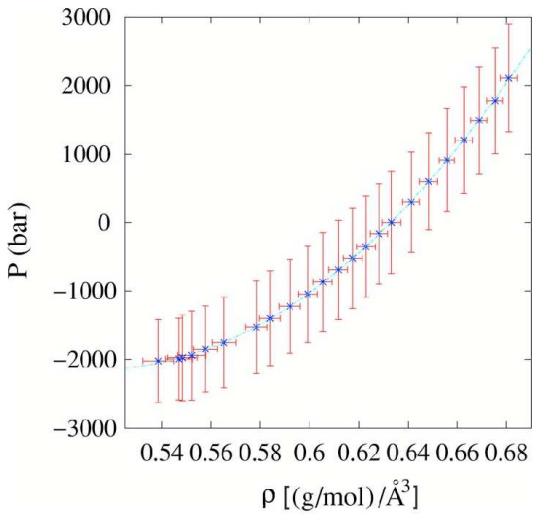
MD-FH Equilibrium

Equation of state $p = p(\rho)$ for argon and water TIP3P, $T = 300K$ [G.Fabritiis et al. PRE, **76** (2007)].

OPEN MD can be used to measure $p = p(\rho)$

argon (LJ) water (TIP3P)

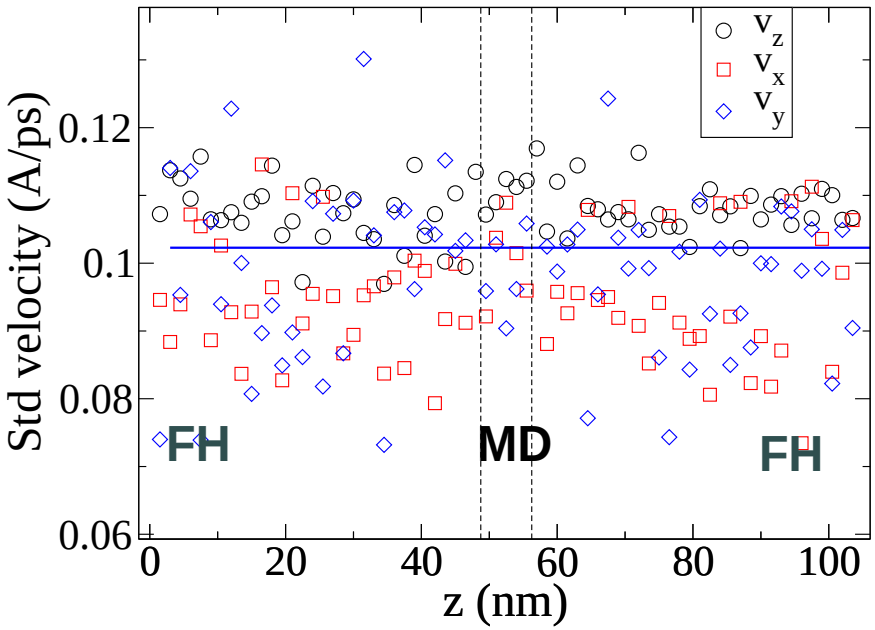




MD-FH Velocity and stress fluctuations

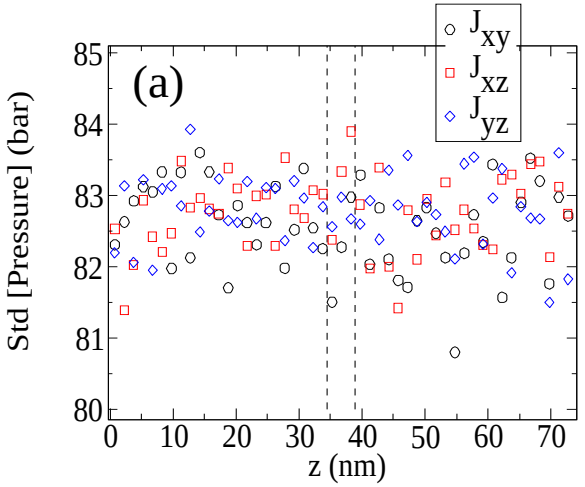
`Standard deviation of velocity` (kinetic temperature)
liquid argon @ $T = 300K$ [RDB and G.Fabritiis et al. PRE, **76** (2007)].

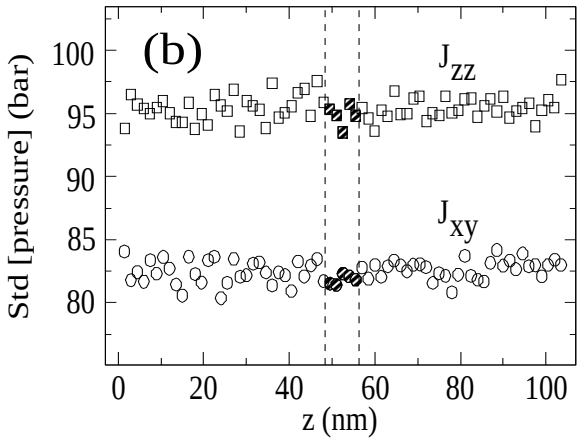
STD velocity



position

STD Stress tensor components





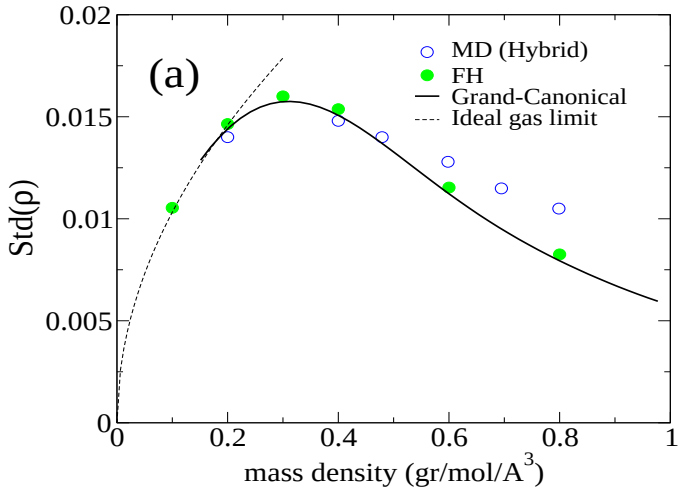
position

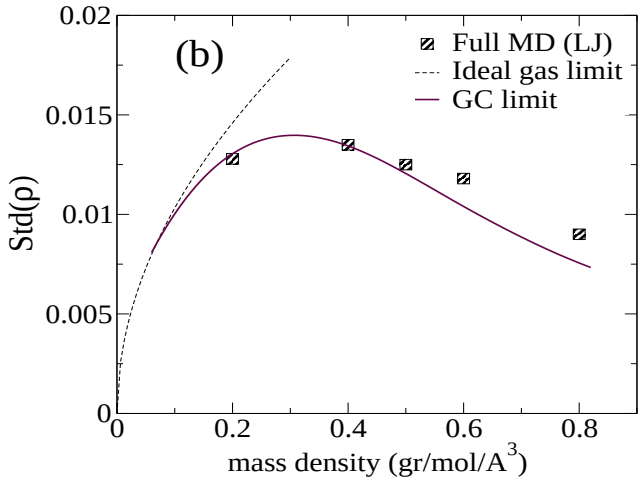
MD-FH Density fluctuations

`Standard deviation of density`

argon at several densities, $T = 300K$

RDB and G.Fabritiis et al. PRE, **76** (2007)





HybridMD

FH

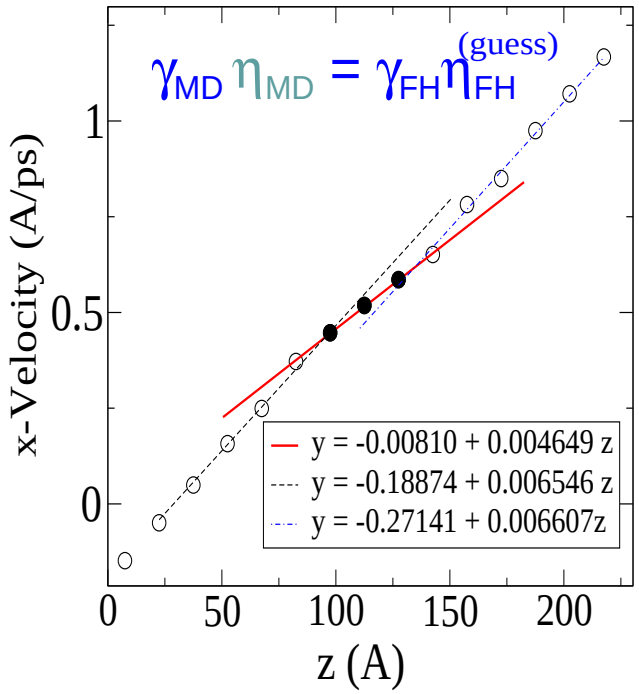
Grand canonical →

full MD

MD-FH **Shear flow**

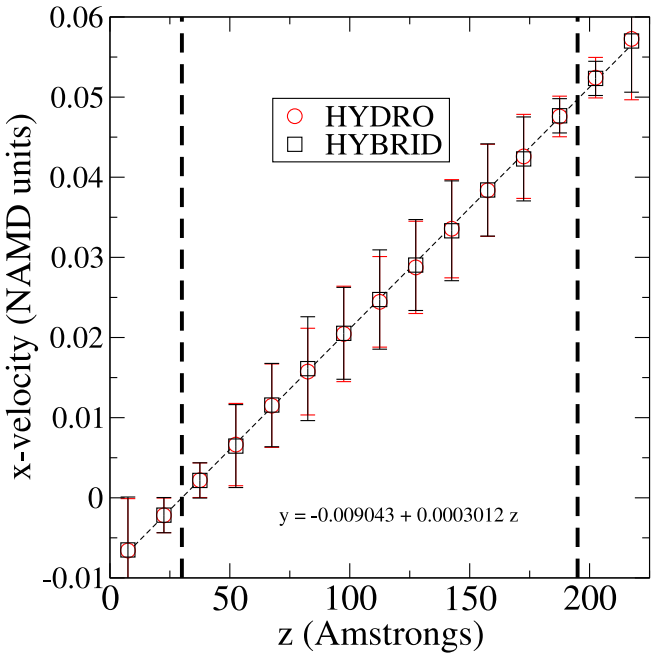
viscosity calibration

hybridMD as a rheometer



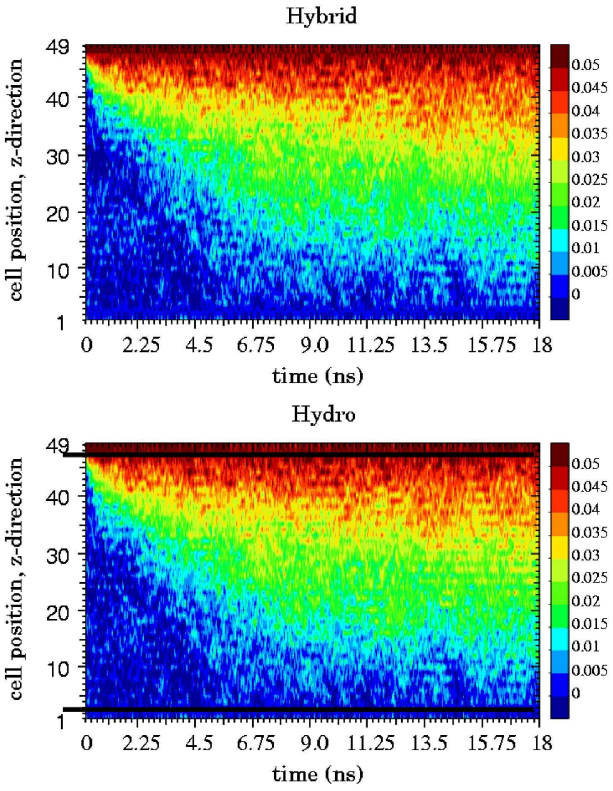
Couette flow

steady solution

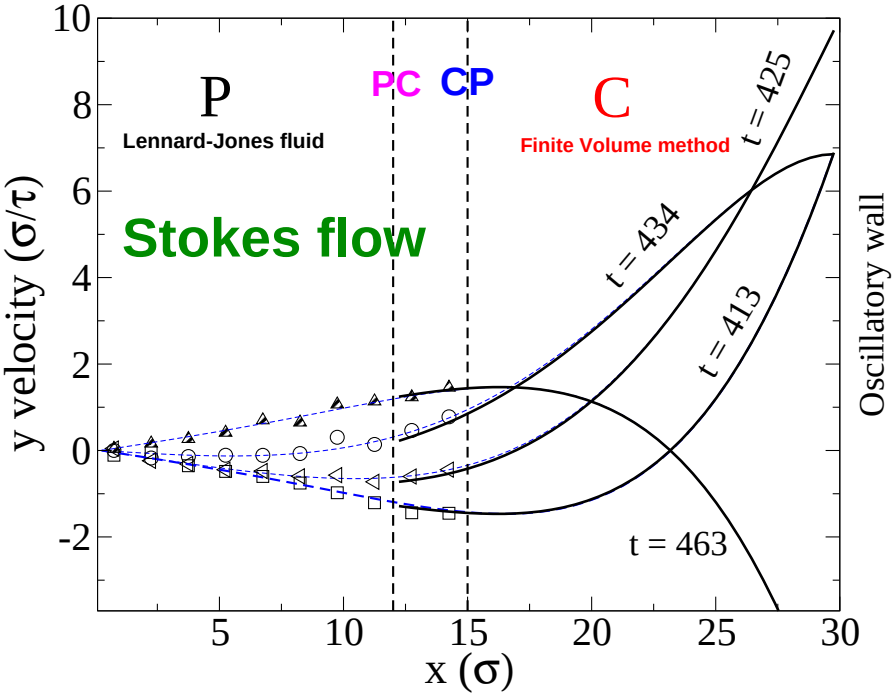


MD-FH **Unsteady shear**

Start-up Couette

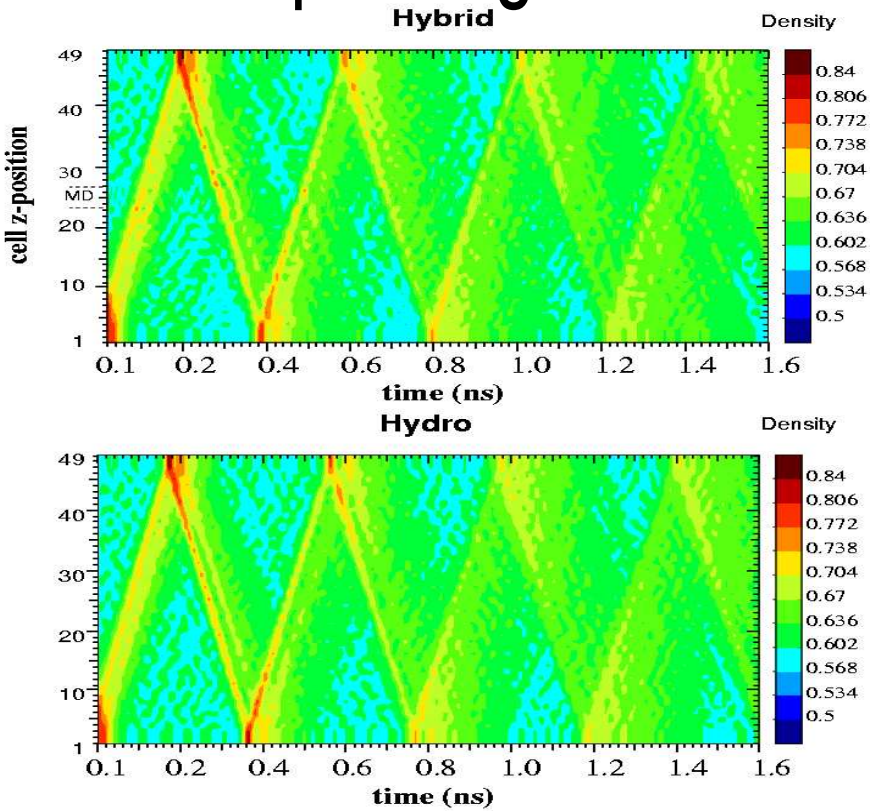


Oscillatory shear

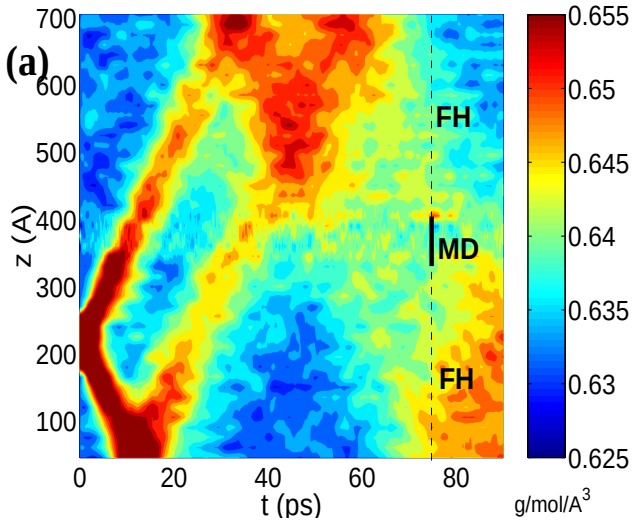


MD-FH **Sound waves**

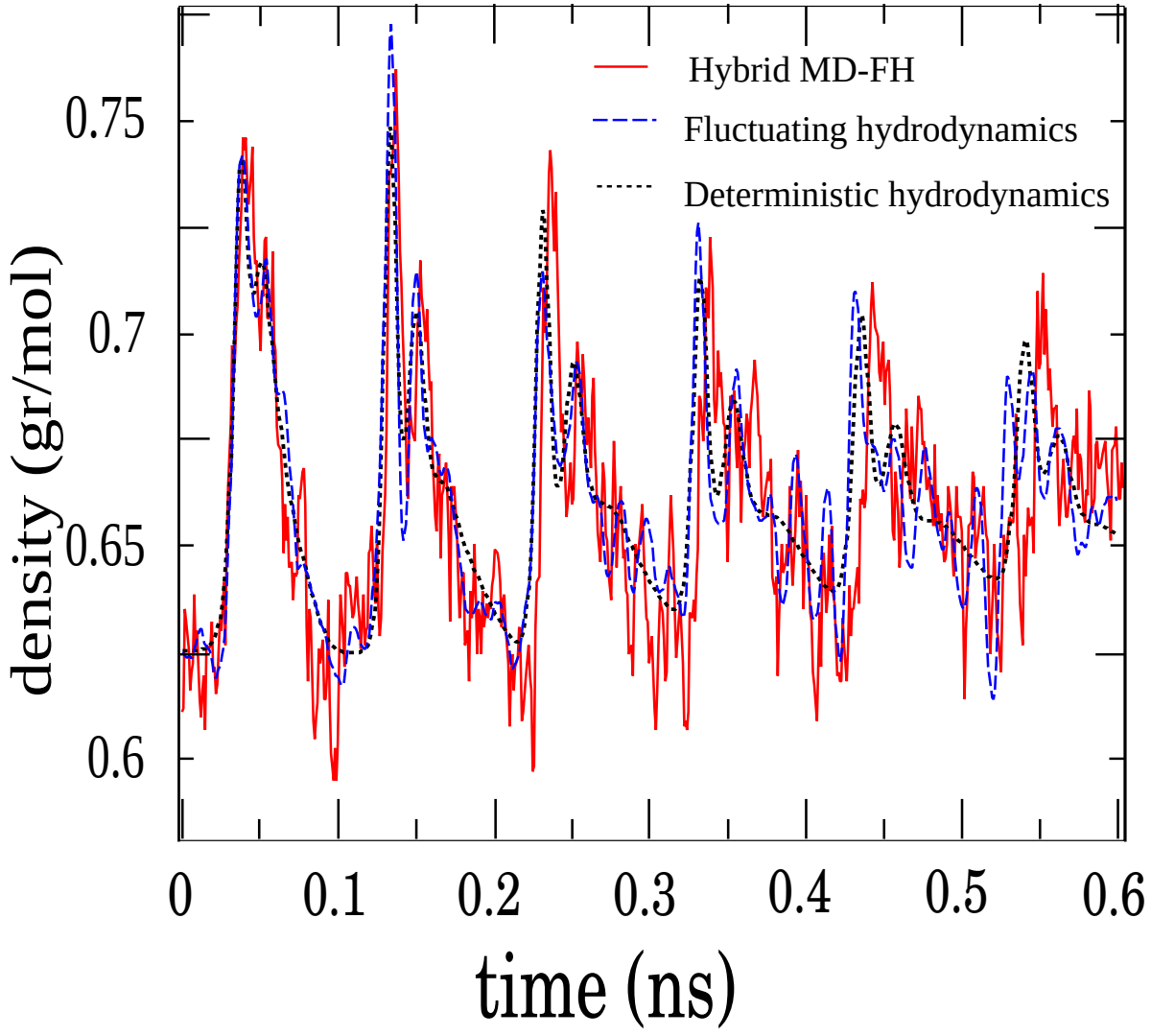
liquid argon



water

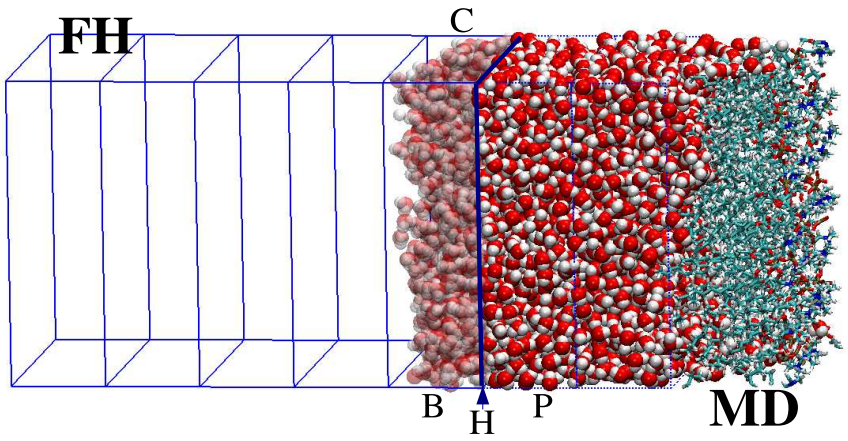


MD-FH **Sound waves: time resolution** ~ 0.02 **ns**

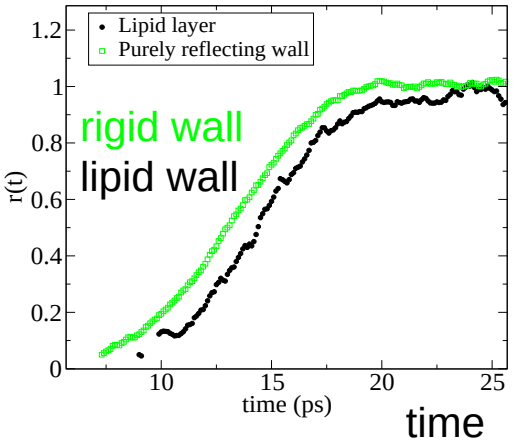


MD-FH **Sound - (soft) mattter interaction**

RDB et al, J. Mech. Engineering Sci. (2008)

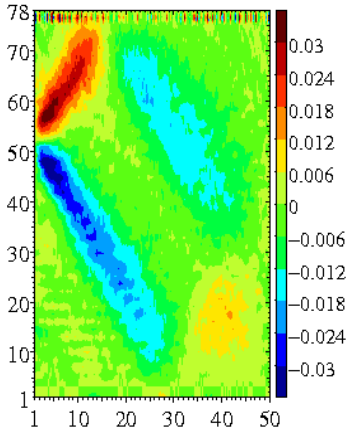


Reflection coefficient

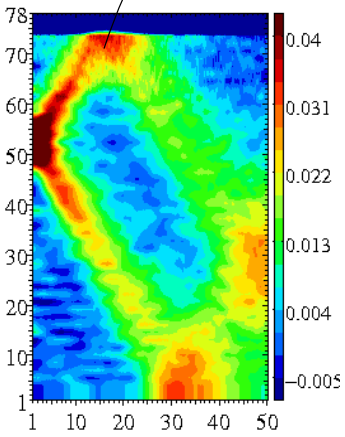


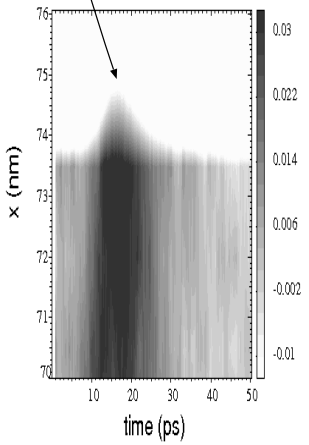
time

velocity

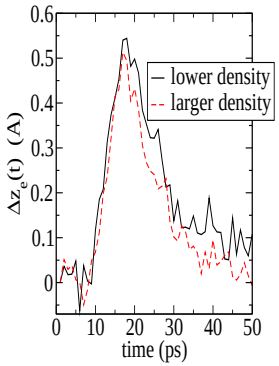


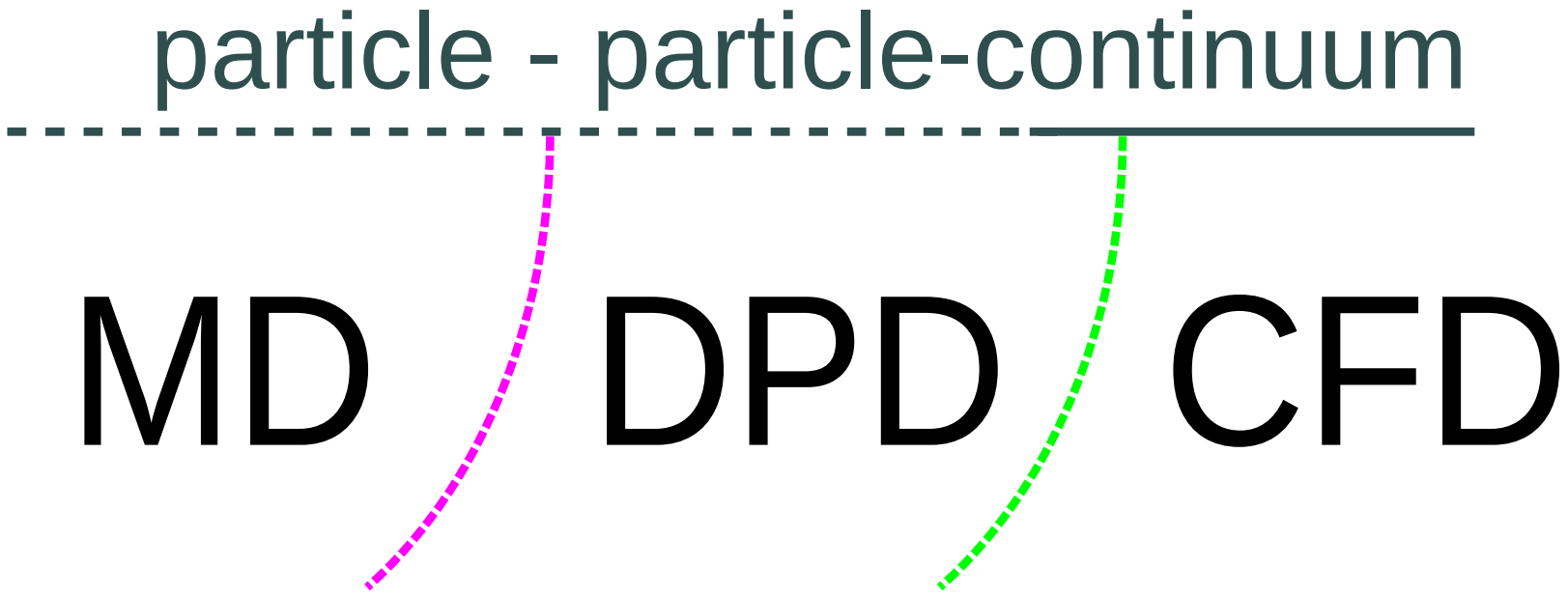
water density





lipids' tail displacement




particle - particle-continuum
MD
DPD
CFD

MD-DPD-CFD

Triple scale coupling

RDB, K. Kremer, M. Praprotnik, J. Chem. Phys, **128** 114110, (2008)

`General motivation`

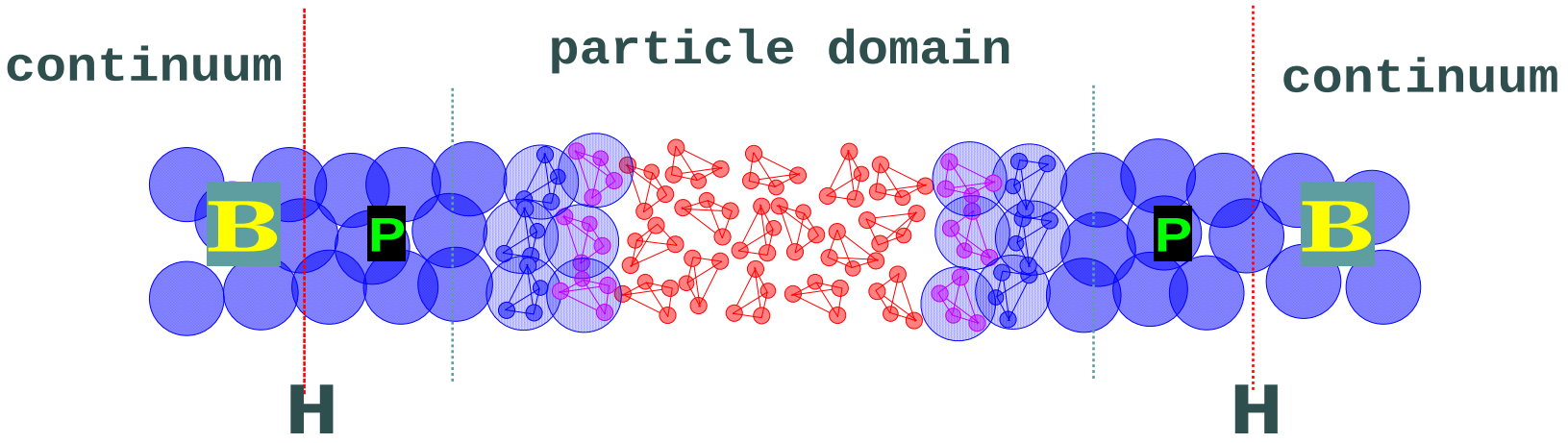
Complex molecules

- Technical issues
  - Generalize the (MD-DPD) AdResS scheme to include **hydrodynamics**
  - Solve the **insertion** of larger molecules in hybridMD
- Applications
  - Phenomena involving flow-matter interaction at multiple length scales complex fluids near surfaces, lubrication, macromolecules in flow,...
  - Grand canonical molecular dynamics involving complex molecules confined systems

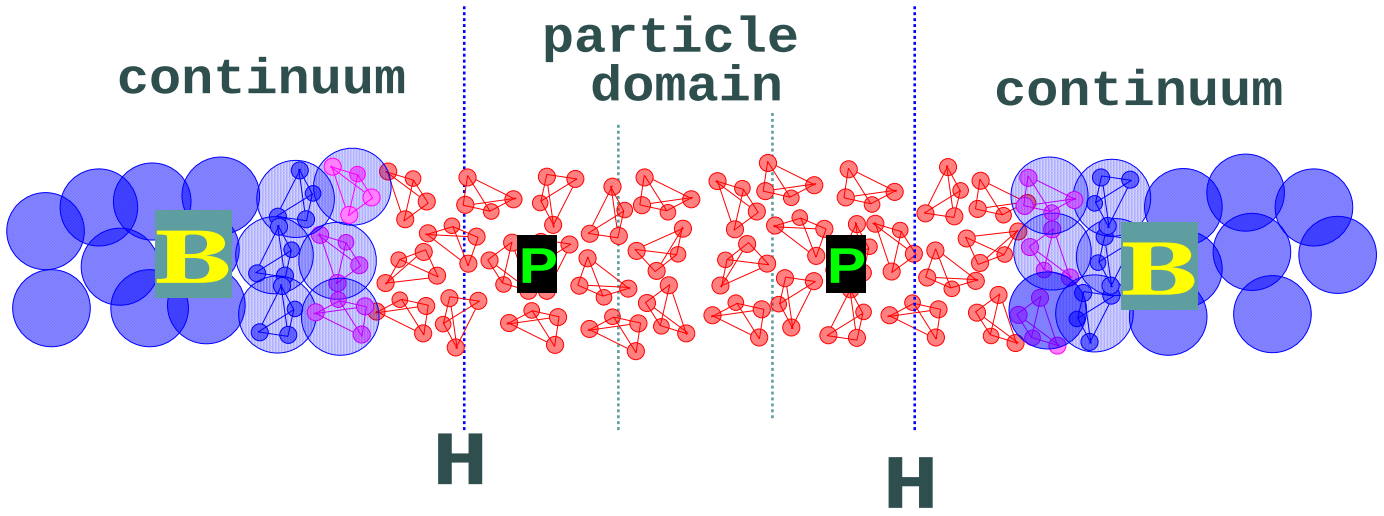
MD-DPD-CFD **Two possible setups**

RDB, K. Kremer, M. Praprotnik, J. Chem. Phys, **128** 114110, (2008)

Homogeneous (CG) buffer



Heterogeneous model buffer



MD-DPD-CFD: **Two possible setups**

RDB, K. Kremer, M. Praprotnik, J. Chem. Phys, **128** 114110, (2008)

- **Homogeneous buffer**
  - `con:` Requires fine tunning of `CG` model
    - Viscosity **or** molecular diffusion coefficient
      Transversal DPD C. Junghans, et al., Soft Matter 4, 156 (2008)
    - Equation of state
  - `pro:` Requires smaller buffer size
  - `pro:` Permits to introduce CG molecular information into the MD (explicit) region (structure, diffusion rates, etc...)

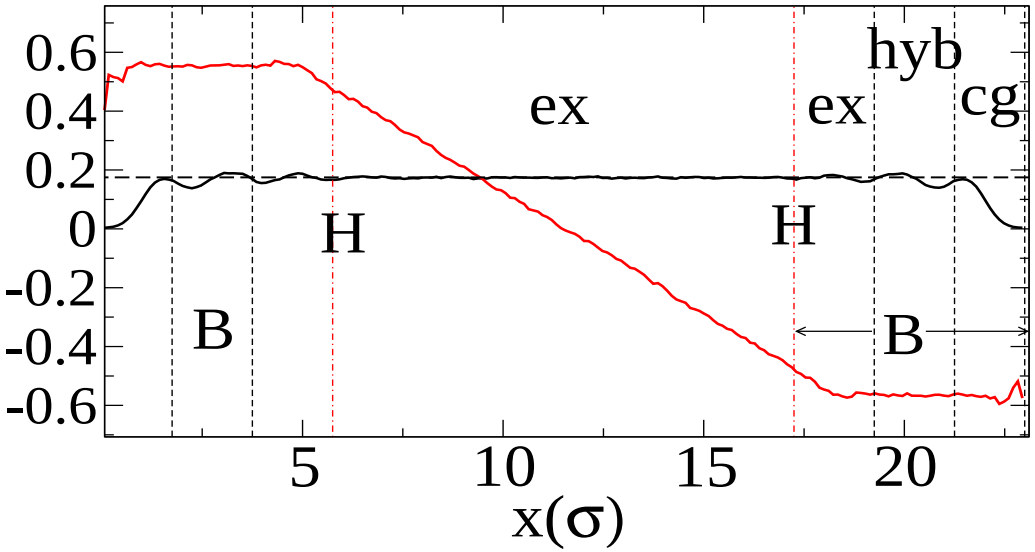
- **Heterogeneous buffer**
  - `con:` Larger buffer size
  - `pro:` The P-cell is fully atomistic (correct viscosity, EOS, fluctuations)
  - `pro:` Does not requires fine tunning of `CG` model and `hyb` models

MD-DPD-CFD: **Shear flow**

Heterogeneous buffer

high density tetraedral liquid under shear

density and velocity profiles

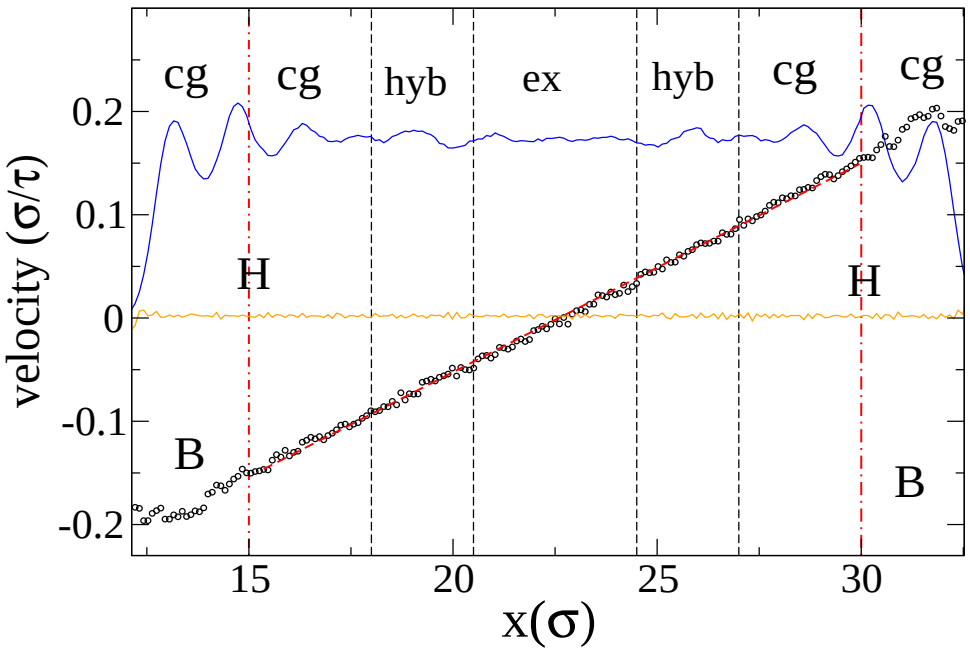


MD-DPD-CFD: **Shear flow**

Homogeneous buffer

high density tetraedral liquid under shear

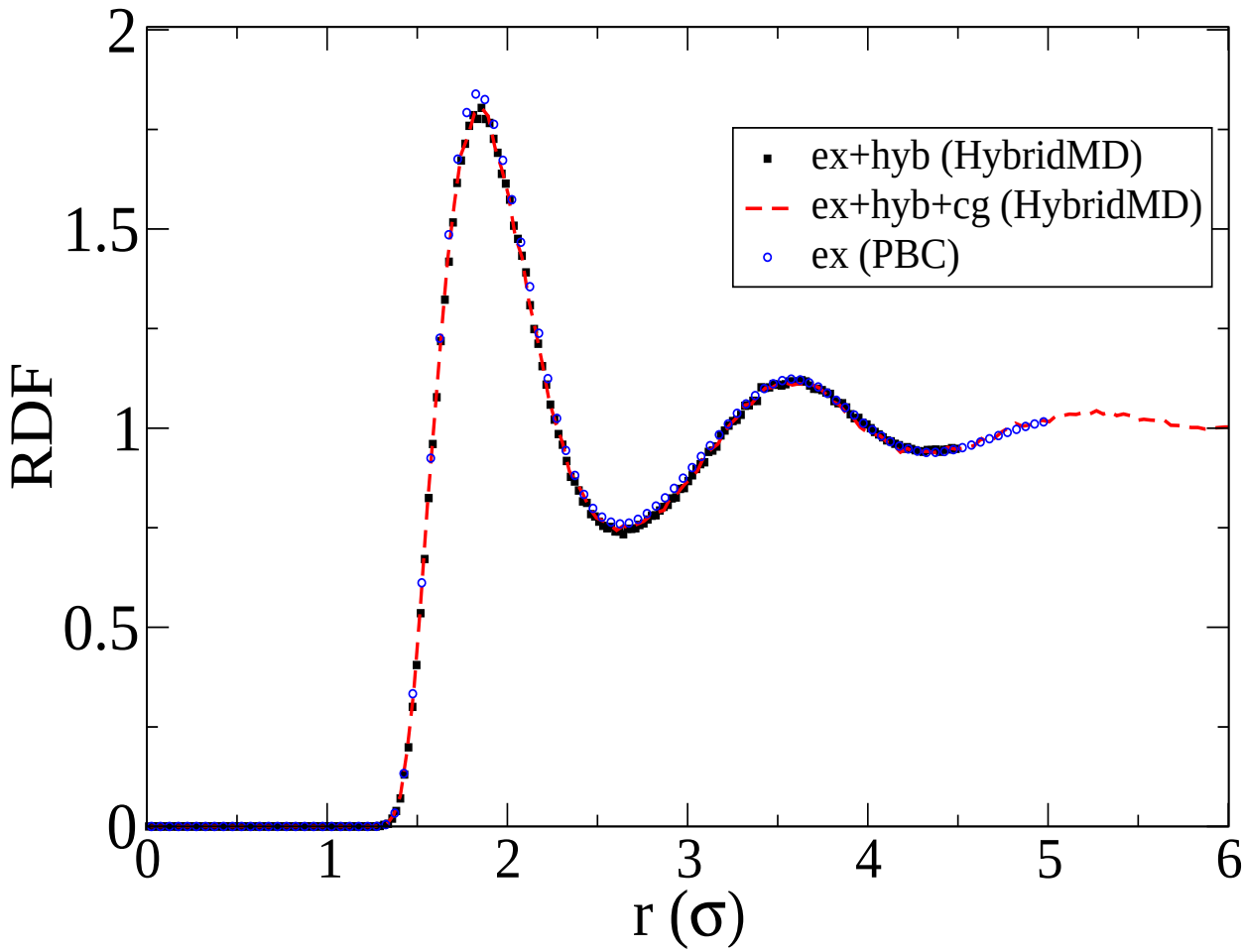
density and velocity profiles



MD-DPD-CFD: **Equilibrium**

liquid structure around the hybrid interface

Radial distribution function
high density tetraedral liquid



MD-DPD-CFD: **Equilibrium: grand canonical**

Mass fluctuations

- Scaled standard deviation of mass $\sigma_N^2/V = \rho k_B T \left(\frac{\partial p}{\partial \rho}\right)_T^{-2}$

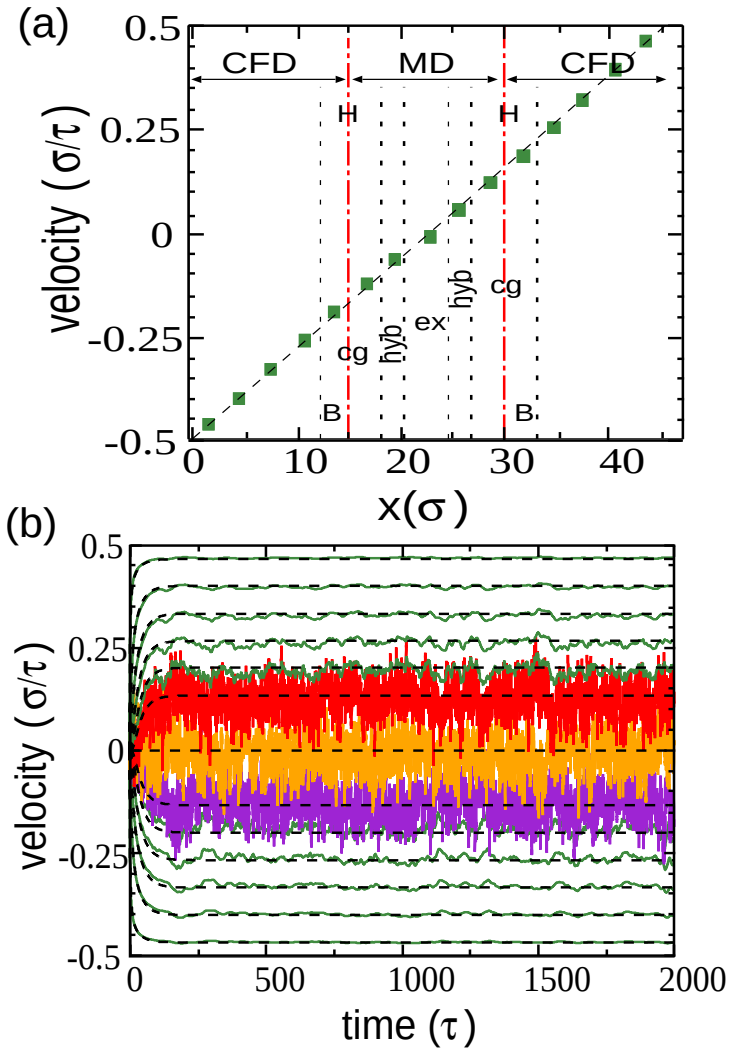
ρ	simulation	Grand canonical
0.1	0.2	0.17
0.175	0.1	0.07

- Standard deviation number of particles in one cell, $V = 15 \times 15 \times 3\sigma^3$ similar values within error bars

Coarse Grained	hyb	atomistic
13.9	14.2	14.5

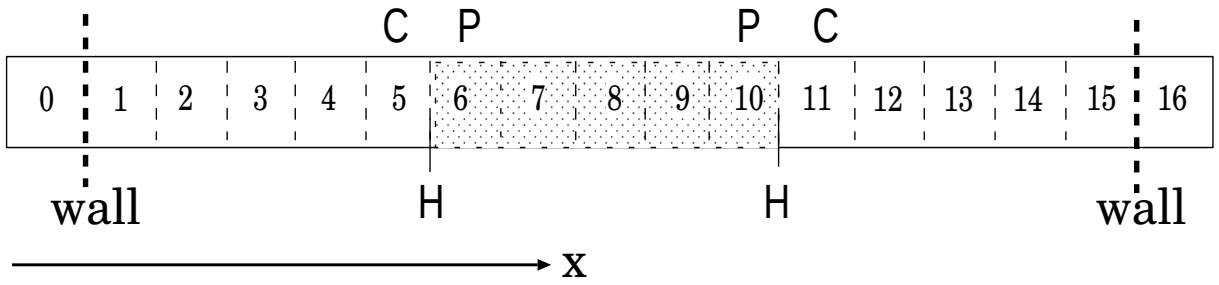
MD-DPD-CFD: **Unsteady flows**

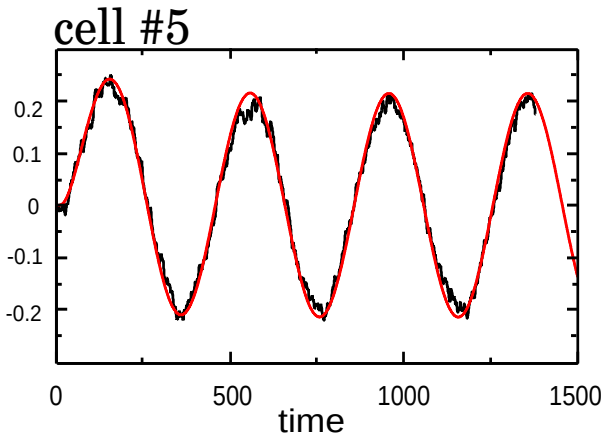
Start Couette flow

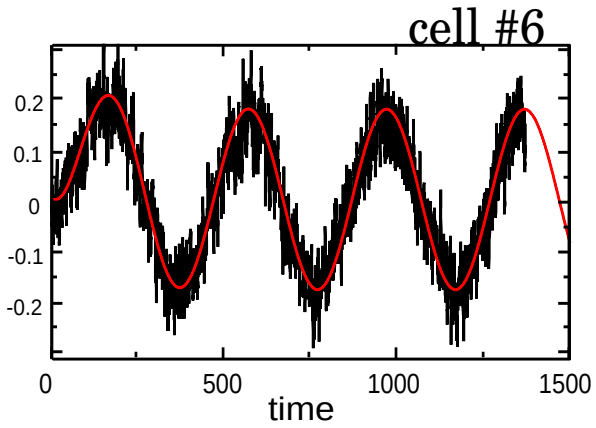


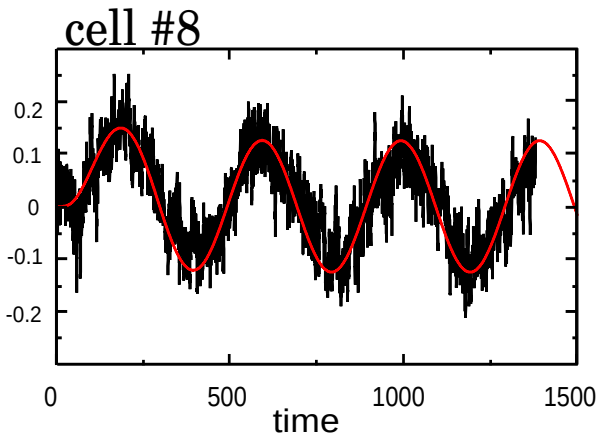
MD-DPD-CFD: **Unsteady flows**

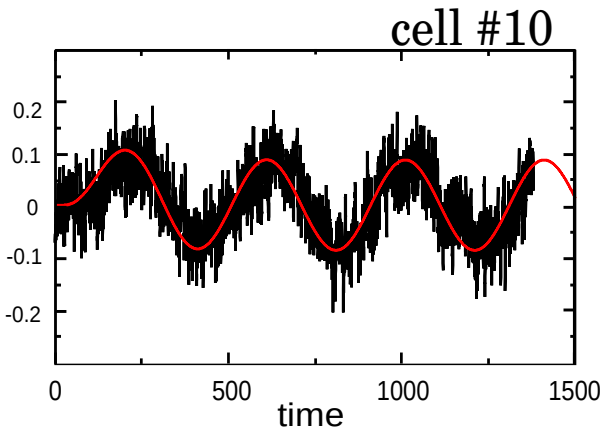
Stokes flow (oscillatory shear)







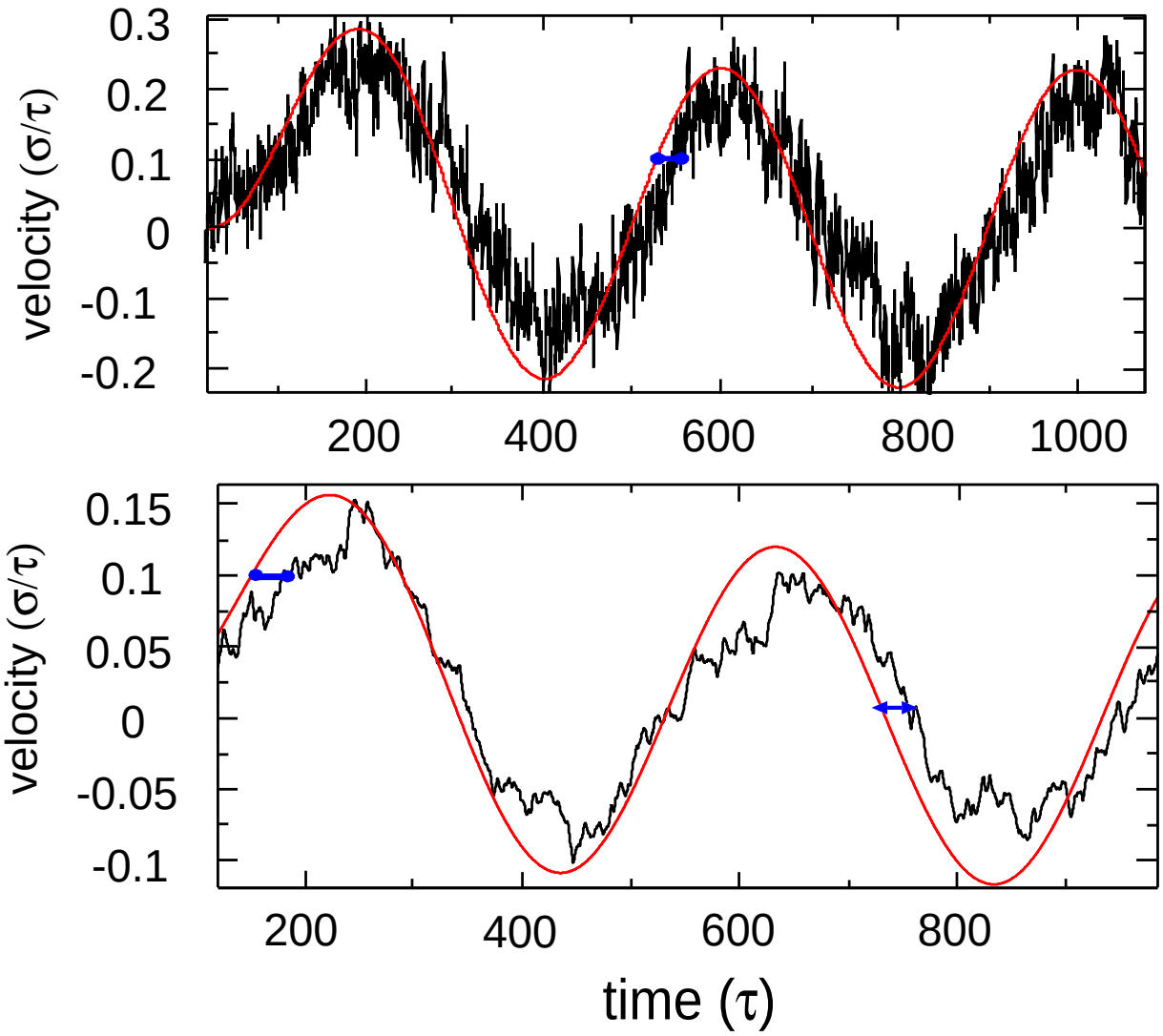




MD-DPD-CFD: **Unsteady flows**

Diffusive delay in long buffers

Delay time (due to momentum diffusion along buffer): $\tau_B \simeq \ell_B^2 \rho/\eta$



Concluding remarks

- Multiscale modeling based on domain decomposition

- Coupling across scales:
  - MD-DPD
    - Proper coarse-grained structure and pressure
    - Diffusive (mass) transport at mesoscale can be (to some extent) matched
  - MD-continuum hydrodynamics; MD-Fluctuating hydrodynamics.
    - Sound, heat and energy transfer
    - Open molecular dynamics (grand canonical μVT and other ensembles)
  - Triple scale model: MD-DPD-continuum
    - Coarse-grained (DPD like) intermediate model
    - Proper hydrodynamics on shear and isothermal sound transport (not heat)
    - Solves insertion of complex molecules in hybrid schemes

Some key authors on the subject

- MD-DPD
  - M. Praprotnik, L. Delle Site, K. Kremer
- MD-continuum hydrodynamics
  - DSMC-CFD: A. Garcia, F. Alexander, B. Alder (AMAR)
  - MD-CFD: E. Flekkoy, Koumoutsakos, Hadjiconstantinou, M. Robbins, Nie, S. Yip
  - MD-FH: G. De Fabritiis, P. Coveney , Delgado-Buscalioni
- Triple scale model: MD-DPD-continuum
  - Delgado-Buscalioni, M. Praprotnik, K. Kremer